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(54) Title: MALODOR REDUCING COMPOSITION CONTAINING AMBER AND MUSK MATERIALS			
(57) Abstract			
Malodor reducing compositions including an amber chemical material and a musk material, and consumer products including the malodor reducing compositions, for example, fabric freshening compositions, hair treating compositions, hard surface cleaning compositions, antiperspirants/deodorants, air freshening compositions, are disclosed. The malodor reducing composition provides a reducing malodor impression on surfaces of, e.g., fabrics, floors, air in confined spaces such as bathrooms, and in consumer products which contain materials that are inherently malodorous, with substantially no odor or only minimal perfume impression.			

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**MALODOR REDUCING COMPOSITION CONTAINING AMBER AND MUSK MATERIALS**

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**TECHNICAL FIELD**

The present invention relates to malodor reducing compositions including an amber chemical material and a musk material, and consumer products including the malodor reducing compositions. The malodor reducing composition is designed to reduce malodor impression on surfaces, such as fabrics, hair, floors, etc., which, for example, have been contaminated with environmental odors such as cigarette smoke odors, cooking smoke odors, and/or that have been wetted with perspiration. The compositions are also useful for reducing malodor in confined air spaces such as bathrooms and kitchens and in reducing malodor in consumer products which contain inherently malodorous ingredients.

**BACKGROUND OF THE INVENTION**

A wide variety of deodorizing compositions are known in the art, the most common of which only contain a perfume to mask the malodor. Odor masking is the intentional concealment of one odor by the addition of another. The preference to the masking perfume is varied greatly, depending on the application, e.g., underarm odor masking, fabric odor masking, bathroom odor masking, etc. Appropriate perfume ingredients need to be selected to connote freshness. Such odor masking composition known to those skilled in the art generally includes strong perfume ingredients and/or includes high volume of perfume composition, in order to achieve odor masking effect that meets consumer needs. However, some consumers do not prefer strong perfumes and/or long lasting perfumes remaining on the surface after treating such odor masking perfume, i.e., such consumers seek an odor masking product that have no odor or very faint odor after applying the product.

Odor modification, in which the odor is changed, e.g., by chemical modification, has also been used. Current malodor modification methods known in the art which do not simply mask odors are oxidative degradation, which uses

oxidizing agents such as oxygen bleaches, chlorine, chlorinated materials such as sodium hypochlorite, chlorine dioxide, etc., and potassium permanganate to reduce malodor, and reductive degradation which uses reducing agents such as sodium bisulfite to reduce malodor. Both of these methods are unacceptable for use on fabrics because they can damage colored fabrics, specifically, they can bleach and discolor colored fabrics.

Other methods of odor control contain actives that are targeted to react with malodors having specific chemical functional groups. Examples of such actives are: biguanide polymers, which complex with organic compounds containing organically bound N and/or S atoms and fatty alcohol esters of methyl methacrylic acid which react with thiols, amines, and aldehydes. A more detailed description of these methods can be found in U.S. Pat. Nos. 2,544,093, 3,074,891, and U.K. Pat. App. No. 941,105, all of said patents and applications are incorporated herein by reference.

Other types of deodorizing compositions known in the art contain antibacterial and antifungal agents which regulate the malodor-producing microorganisms found on the surface to which the deodorizing composition is directed. Many skin deodorant products use this technology. These compositions are not effective on malodors that do not come from bacterial sources, such as cigarette smoke or cooking smoke odors.

Fabric malodor is most commonly caused by environmental odors such as cigarette smoke odor, cooking and/or cooking smoke odors, or body odor. The unpleasant odors are mainly organic molecules which have different structures and functional groups. One type of malodor that is very noticeable, and is commonly found on worn fabrics is low molecular weight, straight-chain, branched, and unsaturated C<sub>6</sub>-C<sub>11</sub> fatty acids that cause axillary odor. See "Analysis of Characteristic Odor from Human Male Axillae", X. Zeng, et al., J. Chem. Ecol., pp. 1469-1492, 1991, incorporated herein by reference. See also, U.S. Pat. No. 4,664,909, Marschner et al., issued May 12, 1987, BE 830,098, published October 1, 1975, and CA 1,088,428, published October 28, 1980, DE 2,803,176, published August 3, 1978, all of said patents and applications incorporated herein by reference. None of the existing art provides all of the advantages and benefits of the present invention.

### SUMMARY OF THE INVENTION

The present invention relates to a malodor reducing composition comprising: (A) an amber chemical material; and (B) a musk material; wherein the total amount of the amber chemical material and the musk material in the composition is at least about 5 % by weight, and wherein the weight ratio of the amber chemical material to the musk material in the composition is from about 100:1 to about 1:100.

The present invention also relates in one aspect to a consumer product, e.g., those selected from the group consisting of: fabric freshening compositions; hair treating compositions; household cleaning compositions; antiperspirants; deodorants; and air freshening compositions; wherein the consumer product comprises the above identified malodor reducing composition.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

### DETAILED DESCRIPTION OF THE INVENTION

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

All percentages are by weight of total composition unless specifically stated otherwise. All ratios are weight ratios unless specifically stated otherwise.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

As used herein, "malodor reducing composition" means a composition which gives the specific impact to sensory evaluators that malodor on the surface of a material or the air in a confined space is reduced after applying such "malodor reducing composition", compared to before such application. As used herein, "sensory evaluators" are the persons having a skill as experts for physical perfume/odor evaluation, and is screened by odor sensory test and has been trained as a sensory evaluator more than a year.

The present invention relates in one aspect to malodor reducing compositions comprising an amber chemical material and a musk material, wherein the total amount of the amber chemical material and the musk material

in the composition is at least about 5 % by weight.

The present invention also relates in one aspect to a consumer product comprising an amber chemical material and a musk material, wherein the total amount of the amber chemical material and the musk material in the product is from about 0.0001 to about 1% by weight.

#### A. Malodor Reducing Composition

The malodor reducing composition of the present invention comprising an amber chemical material and a musk material, wherein the total amount of the amber chemical material and the musk material in the malodor reducing composition is at least about 5 %, preferably at least about 20 %, more preferably at least about 50 %, and wherein the ratio of the the amber chemical material to the musk material in the malodor reducing composition is from about 100:1 to about 1:100, preferably from about 5:1 to 1:60.

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#### Amber Chemical Materials

Amber chemical materials which can be used for the present invention are selected from the group consisting of natural aromatic chemical materials which are isolated as volatile materials from amber grease, synthetic aromatic chemical materials having aroma identical to the aroma of the natural aromatic chemical materials, derivatives thereof, and mixtures thereof.

Non-limiting examples of the amber chemical materials are as follows:

	Structure	MW	CLogP	chemical name
ambroxan	C <sub>16</sub> H <sub>28</sub> O	236	5.3	3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan
grisalva	C <sub>17</sub> H <sub>30</sub> O	250	-	6,6,9a-trimethyl-3a-ethyldodecahydronaphtho[2,1-b]furan
boisisris	C <sub>15</sub> H <sub>26</sub> O	222	4.8	2-ethoxy-9-methylene-2,6,6-trimethylbicyclo[3.3.1]nonane
hydroxyambran	C <sub>15</sub> H <sub>30</sub> O	226	6.2	2-(cyclododecyl)-propan-1-ol
iso e super	C <sub>16</sub> H <sub>26</sub> O	234	4.8	7-acetyl-1,2,3,4,5,6,7,8,-octahydro-1,1,6,7-tetramethylnaphthalene

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trimofix "o"	C <sub>17</sub> H <sub>26</sub> O	246	-	methyl-2,6,10-trimethyl-2,5,9-cyclododecatriene-1-yl ketone
ambrinol	C <sub>13</sub> H <sub>22</sub> O	194	3.8	2,5,5-trimethyl-1,2,3,4,4a,5,6,7-octahydro-2-naphthalenol
timberol	C <sub>15</sub> H <sub>30</sub> O	226	5.9	1-(2,2,6-trimethylcyclohexyl)-3-hexanol
hexahydroirald eine	C <sub>14</sub> H <sub>28</sub> O	212	5.3	$\alpha,\beta,2,2,6-$ pentamethylcyclohexylpropanol
cashmeran	C <sub>14</sub> H <sub>22</sub> O	206	4.0	6,7,-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone
muscogene	C <sub>14</sub> H <sub>24</sub> O	208	4.7	3-oxabicyclo[10.3.0]pentadec-6-ene
cyclamber	C <sub>14</sub> H <sub>26</sub> O	210	5.1	13-oxabicyclo[10.3.0]pentadecane
madrox	C <sub>14</sub> H <sub>28</sub> O	212	5.7	1-methyl-1-methoxycyclododecane
cedroxyde	C <sub>15</sub> H <sub>24</sub> O	220	4.6	4,8,12-trimethyl-13-oxabicyclo[10.1.0]trideca-4,8-diene
boisambrene forte	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	242	5.5	ethoxy methylcyclododecyl ether
cedramber	C <sub>16</sub> H <sub>28</sub> O	236	5.1	cedryl methyl ether
okoumal	C <sub>19</sub> H <sub>28</sub> O <sub>2</sub>	288	6.4	2,4-dimethyl-2-(1,1,4,4-tetramethyltetralin-6yl)-1,3-dioxolane

Among the above examples, especially, ambroxan, grisalva, hydroxyambran, ambrinol, cyclamber, cedroxyde are non-limiting preferable amber chemical materials.

#### 5 Musk Materials

Musk materials which can be used for the present inventions are natural musks or synthetic musks, selected from the group consisting of macrocyclic musks, nitro musks, polycyclic musks, and mixtures thereof.

Non-limiting examples of the musk materials are as follows:

	Structure	MW	ClogP	chemical name
<b>[macrocyclic musks]</b>				
muscone	C <sub>16</sub> H <sub>30</sub> O	238	6.4	3-methylcyclodecanone
civettone	C <sub>17</sub> H <sub>30</sub> O	250	6.5	9-cyclopentadecen-1-one
exaltone	C <sub>15</sub> H <sub>28</sub> O	224	5.9	cyclopentadecanone
ambreton	C <sub>16</sub> H <sub>28</sub> O	236	6.0	5-cyclohexadecen-1-one
pentalide	C <sub>15</sub> H <sub>28</sub> O <sub>2</sub>	240	6.3	cyclopentadecanolide
cyclopentadeca-nolidon	C <sub>15</sub> H <sub>26</sub> O <sub>3</sub>	254	3.8	12-ketocyclopentadecanolide
hexadecanolide	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	254	6.8	cyclohexadecanolide
ambrettolide	C <sub>16</sub> H <sub>28</sub> O <sub>2</sub>	252	6.4	7-cyclohexadecenolide
musk 781	C <sub>15</sub> H <sub>28</sub> O <sub>3</sub>	256	4.4	12-oxa-16-hexadecanolide
musk R-1	C <sub>15</sub> H <sub>28</sub> O <sub>3</sub>	256	4.4	11-oxa-16-hexadecanolide
oxalide	C <sub>15</sub> H <sub>28</sub> O <sub>3</sub>	256	4.4	10-oxa-16-hexadecanolide
musk T	C <sub>15</sub> H <sub>26</sub> O <sub>4</sub>	270	4.6	ethylene brassylate
musk C-14	C <sub>14</sub> H <sub>24</sub> O <sub>4</sub>	256	4.1	ethylene dodecanoate
<b>[polycyclic musks]</b>				
phantolide	C <sub>17</sub> H <sub>24</sub> O	244	5.7	6-acetyl-1,1,2,3,3,5-hexamethylindane
celestolide	C <sub>17</sub> H <sub>24</sub> O	244	5.5	4-acetyl-6-t-butyl-1,1-dimethylindane
traseolide	C <sub>18</sub> H <sub>26</sub> O	258	6.1	5-acetyl-3-isopropyl-1,1,2,6-tetramethylindane
tonalide	C <sub>18</sub> H <sub>26</sub> O	258	6.2	6-acetyl-1,1,2,4,4,7-hexamethyltetralin
galaxolide	C <sub>18</sub> H <sub>26</sub> O	258	6.1	4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydrocyclopentabenzopyran
<b>[nitro musks]</b>				
musk ketone	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	294	3.2	2,6-dinitro-3,5-dimethyl-4-t-butylac tophenone

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musk xylol	C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>6</sub>	297	3.4	2,4,6-trinitro-1,3-dimethyl-5-t-butylbenzene
musk ambrette	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>5</sub>	268	-	2,6-dinitro-3-methoxy-1-methyl-4-t-butylbenzene
musk tibetene	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	266	4.3	2,6-dinitro-3,4,5-trimethyl-t-butylbenzene
musk moskene	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	278	-	1,1,3,3,5-pentamethyl-4,6-dinitroindane

Among the above examples, especially, muscone, exaltone, pentalide, ambrettolide, oxalide, musk T, celestolide, tonalide, galaxolide are non-limiting preferable musk materials. These preferable musk materials generally have ClogP\* of not less than 3.5.

[\*: The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in *Comprehensive Medicinal Chemistry*, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The ClogP values are the most reliable and widely used estimates for this physicochemical property.]

In the present invention, some materials having faint odor are used as solubilizing agent or diluents. Non-limiting examples of these materials are water; C<sub>1</sub>-C<sub>4</sub> monohydric alcohols; C<sub>2</sub>-C<sub>6</sub> polyhydric alcohols; propylene carbonate; liquid polyalkylene glycols; triethyl citrate; isopropyl myristate; benzyl benzoate. These materials are used for, e.g., solubilizing or diluting some solid or viscous ingredients in the compositions of the present invention to, e.g., improve handling and/or formulating, or stabilizing volatile ingredients, e.g., by reducing their vapor pressure.

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#### B. Consumer Products Containing Malodor Reducing Composition

The present invention also relates to consumer products containing the malodor reducing composition wherein the total amount of an amber chemical material and a musk material in the malodor reducing composition is at least about 5 %, preferably at least about 20%, more preferably at least about 50%, and wherein the ratio of the amber chemical material to the musk material in the malodor reducing composition is from about 100:1 to about 1:100, preferably from about

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15.8% 102

5:1 to 1:60.

Non-limiting examples of consumer products which can be applied to the present invention include: fabric freshening compositions; household cleaning compositions; hair treating compositions; antiperspirants; deodorants; and air 5 freshening compositions; wherein the consumer products containing an effective amount of the malodor reducing composition.

The amount of the malodor reducing composition having an amber chemical material and a musk material in the consumer product of the present invention is from about 0.0001% to about 1% by weight, preferably, from about 10 0.001% to about 0.5%, more preferably, from about 0.005% to about 0.1%.

### Surfactant System

The consumer products according to the present invention e.g., household 15 cleaning compositions, antiperspirants, may comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most 20 preferably from 1% to 30% by weight of cleaning compositions in accord with the invention.

Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl 25 phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or 30 branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These 35

0.1-9%  
102

surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro<sup>TM</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C<sub>12</sub>-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing

saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula:



wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Plurafac<sup>TM</sup> LF404 and Pluronic<sup>TM</sup> surfactants, marketed by BASF.

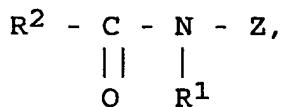
35 Also suitable for us as the nonionic surfactant of the nonionic surfactant

system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally 5 has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this 10 type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures 15 thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates (preferably C<sub>10</sub> avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula:

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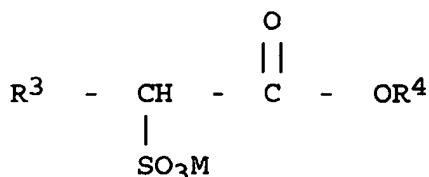
25 wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or 30 mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to 'The 35 Journal of the American Oil Chemists Society', 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow,

palm oil, etc.

The preferred alkyl ester sulfonate surfactant, comprise alkyl ester sulfonate surfactants of the structural formula:

5



10 wherein  $\text{R}^3$  is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof,  $\text{R}^4$  is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, 15 diethanolamine, and triethanolamine. Preferably,  $\text{R}^3$  is C<sub>10</sub>-C<sub>16</sub> alkyl, and  $\text{R}^4$  is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein  $\text{R}^3$  is C<sub>10</sub>-C<sub>16</sub> alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula  $\text{ROSO}_3\text{M}$  wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethylammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C<sub>12</sub>-C<sub>16</sub> are preferred for lower wash temperatures (e.g. below about 50°C) and C<sub>16</sub>-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

30 Other anionic surfactants useful for detergents purposes may also be included in the consumer products of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulfonates, C<sub>8</sub>-C<sub>24</sub> olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C<sub>8</sub>-C<sub>24</sub> alkylpolyglycolethersulfates (containing up to 10 moles of

ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C<sub>6</sub>-C<sub>12</sub> diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those 10 of the formula RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>k</sub>-CH<sub>2</sub>COO-M<sup>+</sup> wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)<sub>m</sub>SO<sub>3</sub>M wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl component, preferably a C<sub>12</sub>-C<sub>20</sub> alkyl or hydroxyalkyl, more preferably C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and 25 about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(1.0)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate (C<sub>12</sub>-C<sub>18</sub>E(2.25)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(3.0)M), and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(4.0)M).

(C<sub>12</sub>-C<sub>18</sub>E(4.0)M), wherein M is conveniently selected from sodium and potassium.

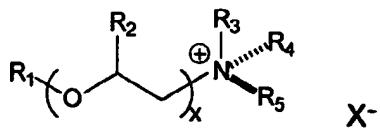
Some preferred compositions of the present invention may contain soaps derived from essentially saturated hydrocarbon chainlengths of from about 8 to about 22 carbon atoms. It is preferred that the soap be the sodium and/or potassium salts, but other soluble soaps can be used. The compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants those already described herein.

Cationic detergents useful herein are those having one long-chain hydrocarbyl group. Examples of such cationic detergents include the ammonium detergents such as alkyltrimethylammonium halogenides, and those detergents having the formula:



wherein R<sup>2</sup> is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R<sup>3</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures thereof; each R<sup>4</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two R<sup>4</sup> groups, -CH<sub>2</sub>CHOH-CHOHCOR<sup>6</sup>CHOHCH<sub>2</sub>OH wherein R<sup>6</sup> is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R<sup>5</sup> is the same as R<sup>4</sup> or is an alkyl chain wherein the total number of carbon atoms of R<sup>2</sup> plus R<sup>5</sup> is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):

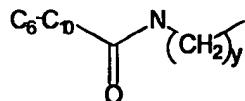


Formula I

whereby R<sub>1</sub> is a short chain length alkyl (C<sub>6</sub>-C<sub>10</sub>) or alkylamidoalkyl of the

- 15 -

formula (II) :



Formula II

5

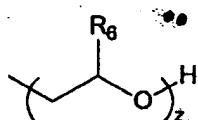
$y$  is 2-4, preferably 3.

whereby  $R_2$  is H or a C1-C3 alkyl,

whereby  $x$  is 0-4, preferably 0-2, most preferably 0,

10 whereby  $R_3$ ,  $R_4$  and  $R_5$  are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxyolated alkyl of the formula III,

whereby  $X^-$  is a counterion, preferably a halide, e.g. chloride or methylsulfate.



15

$R_6$  is C1-C4 and  $z$  is 1 or 2.

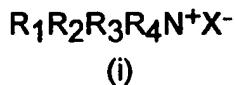
Preferred quat ammonium surfactants are those as defined in formula I

whereby

20  $R_1$  is C8, C10 or mixtures thereof,  $x=0$ ,  
 $R_3$ ,  $R_4 = CH_3$  and  $R_5 = CH_2CH_2OH$ .

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula:

25



wherein  $R_1$  is C8-C16 alkyl, each of  $R_2$ ,  $R_3$  and  $R_4$  is independently C1-C4 alkyl, C1-C4 hydroxy alkyl, benzyl, and  $-(\text{C}_2\text{H}_4)_x\text{H}$  where  $x$  has a value from 2 to 5, and  $X$  is an anion. Not more than one of  $R_2$ ,  $R_3$  or  $R_4$  should be benzyl.

The preferred alkyl chain length for  $R_1$  is C12-C15 particularly where the alkyl

group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R<sub>2</sub>R<sub>3</sub> and R<sub>4</sub> are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

- 5 Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;  
coconut methyl dihydroxyethyl ammonium chloride or bromide;  
decyl triethyl ammonium chloride;  
10 decyl dimethyl hydroxyethyl ammonium chloride or bromide;  
C<sub>12-15</sub> dimethyl hydroxyethyl ammonium chloride or bromide;  
coconut dimethyl hydroxyethyl ammonium chloride or bromide;  
myristyl trimethyl ammonium methyl sulphate;  
lauryl dimethyl benzyl ammonium chloride or bromide;  
15 lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide;  
choline esters (compounds of formula (i) wherein R<sub>1</sub> is  
CH<sub>2</sub>-CH<sub>2</sub>-O-C-C<sub>12-14</sub> alkyl and R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> are methyl).



- 20 di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

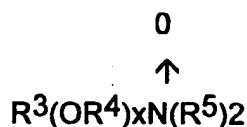
- 25 Ampholytic surfactants can be also used in the consumer products of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

- 30 Zwitterionic surfactants can also be used herein. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of

heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

5        Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula:



wherein R<sup>3</sup> is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R<sup>4</sup> is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R<sup>5</sup> is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R<sup>5</sup> groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C<sub>10</sub>-C<sub>18</sub> alkyl dimethyl amine oxides and C<sub>8</sub>-C<sub>12</sub> alkoxy ethyl dihydroxy ethyl amine oxides.

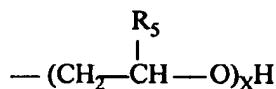
The cleaning composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

35 Suitable primary amines for use herein include amines according to the

formula  $R_1NH_2$  wherein  $R_1$  is a C<sub>6</sub>-C<sub>12</sub>, preferably C<sub>6</sub>-C<sub>10</sub> alkyl chain or  $R_4X(CH_2)_n$ , X is -O-, -C(O)NH- or -NH-,  $R_4$  is a C<sub>6</sub>-C<sub>12</sub> alkyl chain n is between 1 to 5, preferably 3.  $R_1$  alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

5 Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C<sub>8</sub>-C<sub>10</sub> oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

10 Suitable tertiary amines for use herein include tertiary amines having the formula  $R_1R_2R_3N$  wherein R<sub>1</sub> and R<sub>2</sub> are C<sub>1</sub>-C<sub>8</sub> alkylchains or

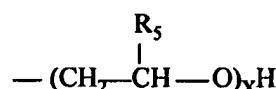


15  $R_3$  is either a C<sub>6</sub>-C<sub>12</sub>, preferably C<sub>6</sub>-C<sub>10</sub> alkyl chain, or  $R_3$  is  $R_4X(CH_2)_n$ , whereby X is -O-, -C(O)NH- or -NH-,  $R_4$  is a C<sub>4</sub>-C<sub>12</sub>, n is between 1 to 5, preferably 2-3.  $R_5$  is H or C<sub>1</sub>-C<sub>2</sub> alkyl and x is between 1 to 6.

$R_3$  and  $R_4$  may be linear or branched ;  $R_3$  alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

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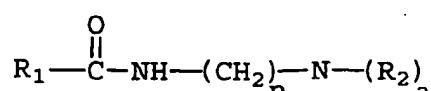
Preferred tertiary amines are  $R_1R_2R_3N$  where R<sub>1</sub> is a C<sub>6</sub>-C<sub>12</sub> alkyl chain, R<sub>2</sub> and R<sub>3</sub> are C<sub>1</sub>-C<sub>3</sub> alkyl or



25

where  $R_5$  is H or CH<sub>3</sub> and x = 1-2.

Also preferred are the amidoamines of the formula



30

wherein R<sub>1</sub> is C<sub>6</sub>-C<sub>12</sub> alkyl; n is 2-4,

preferably n is 3; R<sub>2</sub> and R<sub>3</sub> is C<sub>1</sub>-C<sub>4</sub>

Preferred amines useful herein include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C<sub>8</sub>-10 oxypropylamine, N coco 1-5 3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C<sub>8</sub>-10 amidopropyldimethylamine and C<sub>10</sub> amidopropyldimethylamine.

10 The preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

15

#### Balance Comprising Carrier

The consumer products of the present invention may include balance comprising carrier. The level and species of the carrier are selected according to the compatibility with other components, and desired characteristic of the product. As used herein, the term "balance comprising carrier" includes any of the known balance comprising carriers, generally liquids, including water, C<sub>1</sub>-C<sub>4</sub> monohydric alcohols; C<sub>2</sub>-C<sub>6</sub> polyhydric alcohols; propylene carbonate; liquid polyalkylene glycols; triethyl citrate; isopropyl myristate; benzyl benzoate; and the like; and mixtures thereof.

25 The preferred carrier is aqueous solution, especially, water. The water which is used can be distilled, deionized, or tap water. Water not only serves as the liquid carrier. For example, in the case that consumer product of the present invention is a fabric freshening composition including cyclodextrin (which is fully described below), water not only serves as the liquid carrier of cyclodextrins, but 30 it also facilitates the complexation reaction between the cyclodextrin molecules and any malodorous molecules that are on the fabric when it is treated. It has recently been discovered that water has an unexpected odor controlling effect of its own. It has been discovered that the intensity of the odor generated by some polar, low molecular weight organic amines, acids, and mercaptans is reduced 35 when the odor-contaminated surfaces are treated with an aqueous solution. Not

to be bound by theory, it is believed that water solubilizes and depresses the vapor pressure of these polar, low molecular weight organic molecules, thus reducing their odor intensity. In the case that consumer product is a hair treating composition, for example, a high percentage of volatile solvents of low boiling point and/or propellant are suitably used for product forms aimed to be left on the hair. Volatile solvents useful herein include water, lower alkyl alcohols having from 1 to 3 carbons, and hydrocarbons having from about 5 to about 8 carbons. The preferred volatile solvents are water, ethanol, isopropanol, pentane, hexane, and heptane. The water useful herein include deionized water and water from natural sources containing mineral cations. Deionized water is preferred. In the case that consumer product is an air freshening composition, one or more, volatile solvents are generally included in the composition.

Non-volatile solvents useful herein include alkyl alcohols having more than 3 carbons, and polyhydric alcohols. The polyhydric alcohols useful herein include 1,2-propane diol or propylene glycol, 1,3-propane diol, hexylene glycol, glycerin, diethylene glycol, dipropylene glycol, 1,2-butylene glycol, and 1,4-butylene glycol.

Propellants may be used for consumer products e.g., mousse and hair spray product forms. Propellants, when used in the present invention, are selected depending on variables such as the remainder of components, the package, and whether the product is designed to be used standing or invert.

Propellants useful herein include fluorohydrocarbons such as difluoroethane 152a available from DuPont, dimethylether, and hydrocarbons such as propane, isobutane, n-butane, mixture of hydrocarbons such as LPG (liquid petroleum gas), carbon dioxide, nitrous oxide, nitrogen, and compressed air.

In addition to above, non-limited examples carriers for antiperspirants and deodorants are well known in the art. Some particularly desirable ones are disclosed in U.S. Pat. 4,944,937, McCall, issued Jul. 31, 1990, especially at Col. 2, line 51 through Col. 7, line 11 (Cosmetic Sticks); U.S. Pat. 4,985,238, Tanner, Nunn, Jr., and Luebbe, issued Jan. 15, 1991, especially at Col. 2, line 41 through Col. 3, line 32 and Col. 5, line 45 through Col. 6, line 31 (Low Residue Antiperspirant Sticks); U.S. Pat. 5,019,375, Tanner, Nunn, Jr., and Luebbe, issued May 28, 1991, especially at Col. 3, line 16 through Col. 3, line 35 and Col. 4, line 64 through Col. 7, line 10 (Low Residue Antiperspirant Creams); U.S. Pat.

5,069,897, Orr, issued Dec. 3, 1991, especially at Col. 3, line 1 through Col. 4, line 49 and Col. 5, line 65 through Col. 6, line 64 (Antiperspirant Creams); U.S. Pat. 5,156,834, Beckmeyer, Davis, and Kelm, issued Oct. 20 1992, especially at Col. 4, line 8 through Col. 5, line 64 (Antiperspirant Compositions); U.S. Pat. 5,200,174, Gardlik and Hofrichter, issued Aug. 6 1993, especially at Col. 5, line 16 through Col. 7, line 34 and Col. 10, line 24 through Col. 12, line 44 (Gel Stick Antiperspirant Composition Containing 2-Oxazolidinone Derivative and Process for Making Them); U.S. Pat. 5,284,649, Juneja, issued Feb. 8, 1994, especially at Col. 3, line 55 through Col. 5, line 42 (Deodorant Gel Sticks Containing 1-Hydroxy Pyridinethione Active); and U.S. Pat. 5,298,326, Orr and Newcomer, issued Mar 29, 1994, especially at Col. 6, line 14 through Col. 8, line 21 (Liquid Antiperspirant Composition), all of said patents being incorporated herein by reference. These patents also disclose many of the other ingredients that are useful in antiperspirant and deodorant products.

15 The carriers are generally present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, more preferably from about 10.0% to about 98.0%, of the consumer products of the present invention.

#### Specific Consumer Products

20 The following specific consumer products further describe the preferred examples within the scope of present invention.

##### (i) Fabric Freshening Compositions

The fabric freshening composition of the present invention preferably includes: from about 0.002% to about 1% of a malodor reducing composition of the present invention; from about 0.01% to about 5% of a cyclodextrin; and the balance comprising carrier, wherein the total amount of the amber chemical material and the musk material (1) in the malodor reducing composition is at least about 5% by weight; and (2) in the fabric freshening composition is from about 0.0001% to about 1%.

##### I. Cyclodextrin

30 The fabric freshening composition generally include cyclodextrin. As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six

glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in donut-shaped rings..

Preferably, the cyclodextrins used in the present invention are highly water-soluble such as, alpha-cyclodextrin and/or derivatives thereof, gamma-cyclodextrin and/or derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. Cyclodextrin derivatives include, e.g., those with short chain alkyl groups such as methylated cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a -CH<sub>2</sub>-CH(OH)-CH<sub>3</sub> or a -CH<sub>2</sub>CH<sub>2</sub>-OH group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic cyclodextrins such as those containing 2-hydroxy-3-(dimethylamino)propyl ether, wherein R is CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-N(CH<sub>3</sub>)<sub>2</sub> which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>Cl<sup>-</sup>; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric cyclodextrins such as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in "Optimal Performances with Minimal Chemical Modification of Cyclodextrins", F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49, said references being incorporated herein by reference; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. Nos: 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,678,598, Ogino et al., issued Jul. 7, 1987; 4,638,058, Brandt et al., issued Jan. 20, 1987; and 4,746,734, Tsuchiyama et al., issued May 24, 1988; all of said patents being incorporated herein by reference.

35 Highly water-solubl cyclodextrins ar thos having wat r solubility of at

least about 10 g in 100 ml of water at room temperature, preferably at least about 20 g in 100 ml of water, more preferably at least about 25 g in 100 ml of water at room temperature. The availability of solubilized, uncomplexed cyclodextrins provides for effective and efficient odor control performance. Solubilized, water-soluble cyclodextrin can exhibit more efficient odor control performance than non-water-soluble cyclodextrin when deposited onto surfaces, especially fabric.

Examples of preferred water-soluble cyclodextrin derivatives suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per cyclodextrin is defined as the degree of substitution. Methylated cyclodextrin derivatives typically have a degree of substitution of from about 1 to about 18, preferably from about 3 to 15 about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl- $\beta$ -cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2 methyl groups with a degree of substitution of about 14. A preferred, more commercially available, methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin, commonly known as RAMEB, having different degrees of 20 substitution, normally of about 12.6. RAMEB is more preferred than DIMEB, since DIMEB affects the surface activity of the preferred surfactants more than RAMEB. The preferred cyclodextrins are available, e.g., from Cerestar USA, Inc. and Wacker Chemicals (USA), Inc.

It is also preferable to use a mixture of cyclodextrins. Such mixtures absorb odors more broadly by complexing with a wider range of odoriferous molecules having a wider range of molecular sizes. Preferably at least a portion of the cyclodextrins is alpha-cyclodextrin and its derivatives thereof, gamma-cyclodextrin and its derivatives thereof, and/or derivatised beta-cyclodextrin, more preferably a mixture of alpha-cyclodextrin, or an alpha-cyclodextrin derivative, and derivatised beta-cyclodextrin, even more preferably a mixture of derivatised alpha-cyclodextrin and derivatised beta-cyclodextrin, most preferably a mixture of hydroxypropyl alpha-cyclodextrin and hydroxypropyl beta-cyclodextrin, and/or a mixture of methylated alpha-cyclodextrin and methylated beta-cyclodextrin.

For controlling odor on fabrics, the composition is preferably used as a

spray. It is preferable that usage of fabric freshening compositions of the present invention contain low levels of cyclodextrin so that a visible stain does not appear on the fabric at normal usage levels. Preferably, the solution used to treat the surface under usage conditions is virtually not discernible when dry. Typical 5 levels of cyclodextrin in usage compositions for usage conditions are from about 0.01% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.5% to about 2% by weight of the composition. Compositions with higher concentrations can leave unacceptable visible stains on fabrics as the solution evaporates off of the fabric. This is especially a problem on thin, 10 colored, synthetic fabrics. In order to avoid or minimize the occurrence of fabric staining, it is preferable that the fabric be treated at a level of less than about 5 mg of cyclodextrin per gram of fabric, more preferably less than about 2 mg of cyclodextrin per gram of fabric. The presence of the surfactant can improve appearance by minimizing localized spotting.

15 Concentrated compositions can also be used in order to deliver a less expensive product. When a concentrated product is used, i.e., when the level of cyclodextrin used is from about 3% to about 20%, more preferably from about 5% to about 10%, by weight of the concentrated composition, it is preferable to dilute the concentrated composition before treating fabrics in order to avoid staining. Preferably the concentrated cyclodextrin composition is diluted with 20 about 50% to about 6000%, more preferably with about 75% to about 2000%, most preferably with about 100% to about 1000% by weight of the concentrated composition of water. The resulting diluted compositions have usage concentrations of cyclodextrin as discussed hereinbefore, e.g., of from about 25 0.1% to about 5%, by weight of the diluted composition.

## II. Optional Ingredients for Fabric Freshening Compositions

30 Optionally, fabric freshening compositions of the present invention may include: (a) cyclodextrin-compatible surfactant (e.g., block copolymers of ethylene oxide and propylene oxide, preferable non-limiting examples includes polyalkyleneoxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene side chains); (b) cyclodextrin compatible antimicrobial active (e.g., biguanides and quaternary compounds); (c) low molecular weight polyols (e.g., ethylene glycol, propylene glycol and/or 35 glycerol); (d) optional aminocarboxylate chelators (e.g.,

ethylenediaminetetraacetic acid (EDTA), hydroxyethylene-diaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof); (e) metal salts (e.g., copper salts, zinc salts, and mixtures thereof); (f) humectant (e.g., glycerine, 5 inorganic hygroscopic material); (g) adjunct odor-controlling materials; (h) chelating agents; (i) antistatic agents; (j) insect and moth repelling agents; (k) colorants; (l) antioxidants, and mixtures thereof. The definitions and non-limiting examples of the above (a) thorough (e) is described in US Application No. 08/871576 (filed June 9, 1997).

10 Incorporating adjunct odor-controlling materials can enhance the capacity of the cyclodextrin to control odors as well as broaden the range of odor types and molecule sizes which can be controlled. Such materials include, for example, metallic salts, water-soluble cationic and anionic polymers, zeolites, water-soluble bicarbonate salts, and mixtures thereof.

15 This list of optional ingredients is not meant to be exclusive, and other optional components can be utilized.

#### (ii) Household Cleaning Composition

20 The household cleaning composition of the present invention generally includes: from about 0.002% to about 1% of a malodor reducing composition of the present invention; from about 0.01% to about 60% of a surfactant; an adjunct ingredient selected from the group consisting of abrasives, builders, bleaches, bleach boosters, bleach activators, clays, thickeners, dispersants, enzymes, dyes, colorants, filler salts, hydrotropes, enzymes, preservatives, anti-oxidants, 25 chelants, stabilizers, germicides, fungicides, solvents, photodisinfectants, and mixtures thereof; and the balance comprising carrier, wherein the total amount of the amber chemical material and the musk material (1) in the malodor reducing composition is at least about 5 % by weight; (2) and in the household cleaning composition is from about 0.0001% to about 1%.

30 Non-limited preferable examples of household cleaning compositions of the present invention include : hard surface cleaners; laundry detergent cleaners for wall, carpet, flooring, tatami-mat, screen door, window screen, furniture, household appliances and/or the like.

#### I. ADJUNCT INGREDIENTS

35 Household cleaning compositions of the present invention can adjunct

ingredients. Examples of adjunct ingredients are abrasives, builders, bleaches, bleach boosters, bleach activators, clays, thickeners, dispersants, enzymes, dyes, colorants, filler salts, hydrotropes, enzymes, preservatives, anti-oxidants, chelants, stabilizers, germicides, fungicides, solvents, photodisinfectants, buffers, 5 solvents, and mixtures thereof. This list is not meant to be totally inclusive or exclusive of materials that are compatible for use in the present invention.

The compositions of the present invention can optionally include one or more other hard surface cleaning adjunct materials, carriers, solvents or other materials for assisting or enhancing cleaning performance, treatment of the 10 substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes, etc.).

#### Builders

Builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Preferable are builders that have reduced 15 filming/streaking characteristics at the critical levels of the compositions of the present invention. Addition of specific surfactant builders at critical levels further improves cleaning without the problem of filming/streaking that usually occurs when surfactant builders are added to hard surface cleaners. In light of the improvement displayed by the compositions of the present invention, however, 20 the need for builders to prevent filming and streaking is reduced. Inorganic as well as organic builders can be used.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 0.1% builder. Liquid formulations typically 25 comprise from about 0.1% to about 5%, more typically about 0.2% to about 2%, by weight, of surfactant builder. Lower or higher levels of builder, however, are not meant to be excluded.

Builders suitable for use in the compositions of the present invention include polycarboxylates and phosphates as well as others cited hereinafter. 30 Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. 35 Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether

polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylene-diamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance due to their availability from renewable resources and their biodegradability. Oxydisuccinates are also especially useful in the compositions and combinations of the present invention.

A preferred polycarboxylate builder is iminodisuccinate. Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Suitable additional optional detergent builders include salts of ethylenediaminetetraacetic acid (hereinafter EDTA), citric acid, nitroacetic acid, (hereinafter NTA), sodium carboxymethylsuccinic acid, sodium N-(2-hydroxypropyl)-iminodiacetic acid, and N-diethyleneglycol-N,N-diacetic acid (hereinafter DIDA). The salts are preferably compatible and include ammonium, sodium, potassium and/or alkanolammonium salts. The alkanolammonium salt is preferred as described hereinafter. A preferred detergent builder are the mixtures citric acid/acetate and bicarbonate/carbonate, more preferred bicarbonate/carbonate.

The additional optional surfactant builders, when present, are typically at levels of from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.3%, most preferably from about 0.02% to about 0.15%. The level of these additional builders, present in the wash solution of hard surfaces that comprise glass should be less than about 0.2%.

35 Chelating Agents

The hard surface cleaning compositions herein may also optionally contain one or more transition metal chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

#### Optional Solvents

Optionally, the compositions of the present invention further comprise one or more solvents. Solvents are broadly defined as compounds that are liquid at temperatures of 20°C-25°C and which are not considered to be surfactants. One of the distinguishing features is that solvents tend to exist as discrete entities rather than as broad mixtures of compounds. Solvents of this invention contain from about 1 carbon atom to about 35 carbon atoms, and contain contiguous linear, branched or cyclic hydrocarbon moieties of no more than about 8 carbon atoms. Examples of suitable solvents for the present invention include, methanol, ethanol, propanol, isopropanol, 2-methyl pyrrolidinone, benzyl alcohol and morpholine n-oxide. Preferred among these solvents are methanol and isopropanol.

In a preferred embodiment of the invention, the solvents are selected from the group of compounds comprising ether derivatives of mono-, di- and tri-ethylene glycol, propylene glycol, butylene glycol ethers, and mixtures thereof.

The molecular weights of the preferred solvents are less than about 350, more preferably between about 100 and about 300, even more preferably between about 115 and about 250. Examples of preferred solvents include, for example, mono-ethylene glycol n-hexyl ether, mono-propylene glycol n-butyl ether, and tri-propylene glycol methyl ether. Ethylene glycol and propylene glycol ethers are commercially available from the Dow Chemical Company under the tradename "Dowanol" and from the Arco Chemical Company under the tradename "Arcosolv". Other preferred solvents including mono- and di-ethylene glycol n-hexyl ether are available from the Union Carbide company. Preferred solvents according to this invention are present in from about 1% to about 10%, more preferably from about 2% to about 8%, most preferably from about 3% to about 7%, by weight of the hard surface cleaner composition.

#### Dyes

Optionally, dyes may be included at levels of from about 0.001% to 0.5%. Examples of suitable dyes are Alizarine Light Blue B (C.I. 63010), Carta Blue VP (C.I. 24401), Acid Green 2G (C.I. 42085), Astrogen Green D (C.I. 42040), Supranol Cyanine 7B (C.I. 42675, Maxilon Blue 3RL (C.I. Basic Blue 80), Drimarine Blue Z-RL (C.I. Reactive Blue 18), Alizarine Light Blue H-RL (C.I. Acid Blue 182), FD&C Blue No. 1 and FD&C Green No. 3. (See the patents of Kitko, U.S. Pat. No. 4,248,827 issued February 3, 1981 and U. S. Pat. No. 4,200,606, issued April 29, 1980, both incorporated herein by reference.) C.I. refers to Color Index.

#### Polymeric Dispersing Agents

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein. Suitable polymeric dispersing agents include polymeric polycarboxylates, polystyrene sulfonates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric

polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay

soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

- Polyaspartate and polyglutamate dispersing agents may also be used.
- 5 Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

#### Abrasives

An essential component of many solid or viscous semi-solid hard surface cleaning compositions is the abrasive material added to facilitate the action of

10 scouring. Abrasive scouring cleansers provide a convenient and useful means for carrying out the sanitizing of porcelain and tile surfaces, especially tubs, showers and toilet bowls. The particulate abrasive material within such compositions serves to abrade and loosen soil adhering to hard surfaces and further serves to create more intimate contact between hard surface stain and

15 the surfactant and/or bleaching agents also present in the cleansing compositions.

Abrasive cleaners have traditionally contained water-insoluble, relatively hard, particulate mineral material as the abrasive agent. The most common such abrasive agent is finely divided silica sand having particle size varying between

20 about 1 and 300 microns and specific gravity of about 2.1 or higher. While such material is generally very effective in scouring soil and stains from the surfaces being treated, abrasive material of this type tends to be difficult to rinse away from the toilet bowl, shower or bathtub surface.

It has been discovered that abrasive compositions of this desired type can

25 be realized by utilizing a particular type of expanded perlite abrasive in combination with the surfactants, filler material, and other optional scouring material ingredients listed herein. The abrasive materials suitable to the present invention are those contained in U.S. Pat. No. 4,051,056, Hartman, issued September 27, 1977 and included herein by reference.

30

#### (iii) Hair Treating Composition

The hair treating composition of the present invention generally includes: from about 0.002% to about 1% of a malodor reducing composition of the present invention; from about 0.01% to about 10% of a fixative polymer; and the balance comprising water, wherein the total amount of the amber chemical

material and the musk material (1) in the malodor reducing composition is at least about 5 % by weight; and (2) in the hair treating composition is from about 0.0001% to about 1%.

Non-limited Preferable examples of hair treating compositions of the 5 present invention include : mousse, hair spray, hair mist, gel, and hair tonic.

When the hair treating composition is a hair spray, tonic, gel, or mousse the preferred solvents include water, ethanol, volatile silicone derivatives, and mixtures thereof. The solvents used in such mixtures can be miscible or immiscible with each other.

10 I. Fixative Polymers

Hair Treating Compositions herein generally include a fixative polymer. The fixative polymers useful herein are those which provide a styling or setting benefit to the hair, including

15 fixative polymers, anionic fixative polymers, cationic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers. The fixative polymers in this section can be distinguished from the conditioning agent polymers mentioned above and the suspending agent polymers as mentioned below, in that they have a film-forming characteristic, and that the 3% aqueous solution of fixative polymers herein provide a viscosity of no more than about 2,000 cps.

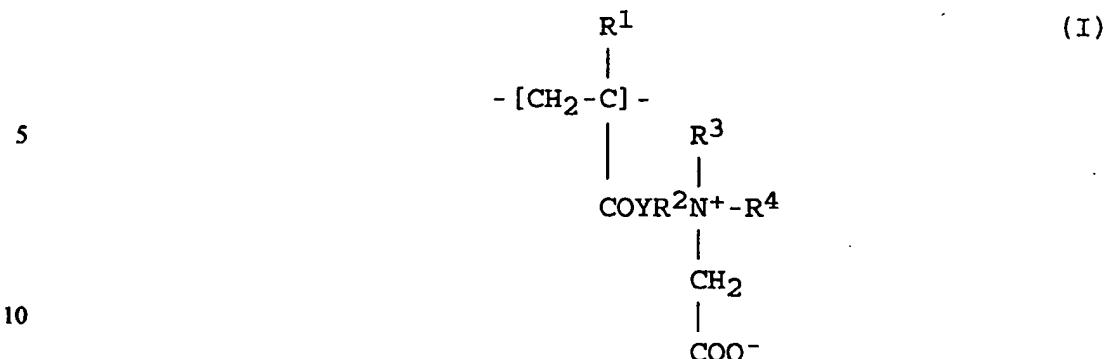
20 The fixative polymers, when present, are preferably included at a level of from about 0.01% to about 10% by weight of the composition. When two or more fixative polymers are used, each fixative polymer does not exceed about 5% by weight of the composition.

Amphoteric Fixative Polymer

25 The amphoteric fixative polymers useful herein include betainized amphoteric polymers as described in (1) and (2) below, and non-betainized polymers as described in (3) and (4) below.

Betainized Amphoteric Fixative Polymers

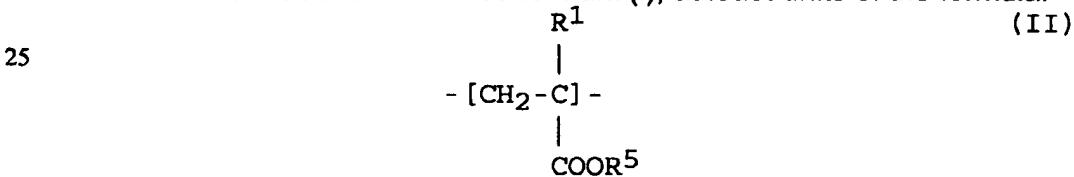
30 (1) Useful herein are polymers of betainized dialkylaminoalkyl (meth)acrylate or dialkylaminoalkyl (meth)acrylamide containing at least units of the formula:



wherein  $\text{R}^1$  denotes a hydrogen atom or a methyl group,  $\text{R}^2$  denotes an alkylene group having 1 to 4 carbon atoms, Y denotes O or  $-\text{NH}-$  and  $\text{R}^3$  and  $\text{R}^4$  independently of one another denote hydrogen or alkyl having 1 to 4 carbon atoms, and one cationic derivative consisting of a cationic surfactant containing at least one nitrogen atom joined to one or more fatty chains and optionally quaternised, or consisting of a cationic polymer of the polyamine, polyaminopolyamide or poly-(quaternary ammonium) type, the amine or ammonium groups forming part of the polymer chain or being joined thereto.

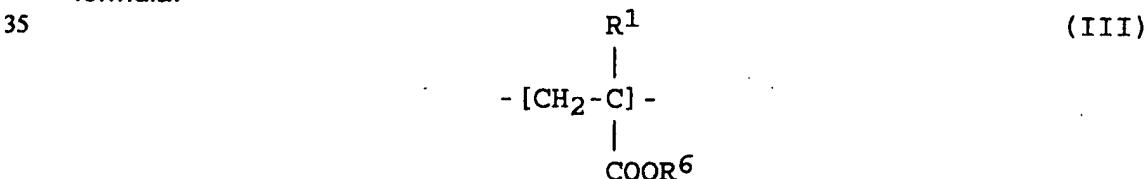
15 These polymers usually have a molecular weight of 500 to 2,000,000.

20 The amphoteric polymers containing units corresponding to the above formula (I) are generally in the form of copolymers which contain, in addition to the units of the above mentioned formula (I), at least units of the formula:



wherein  $\text{R}^1$  is as defined above and  $\text{R}^5$  represents an alkyl or alkenyl radical having from 4 to 24 carbon atoms or a cycloalkyl radical having from 4 to 24 carbon atoms.

30 It is also possible to use terpolymers, tetrapolymers or pentapolymers which contain, in addition to the units (I) and (II) defined above, units of the formula:

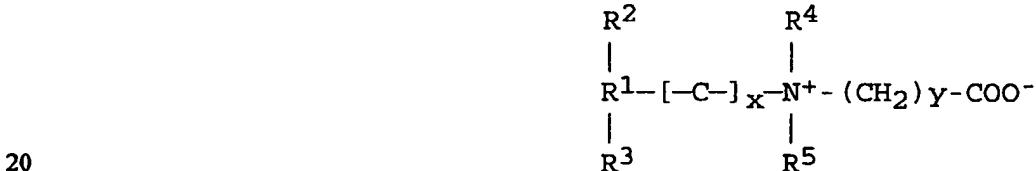


wherein R<sup>6</sup> preferably denotes an alkyl or alkenyl group having 1 to 3 carbon atoms and R<sup>1</sup> is as defined above.

The units of the formula (I) are preferably present in an amount of 25 to 45% by weight, units of the formula (II) are preferably present in an amount of 5 to 65% by weight, and units of the formula (III) are preferably present in an amount up to 50% by weight, relative to the total weight of the polymer.

A particularly preferred polymer is the copolymer containing units of the formulae (I), (II) and (III) in which Y denotes an oxygen atom, R<sup>2</sup> denotes the group -C<sub>2</sub>H<sub>4</sub>-, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> denote methyl, R<sup>5</sup> denotes an alkyl group having 4 to 18 carbon atoms and R<sup>6</sup> denotes an alkyl group having 1 to 3 carbon atoms. The average molecular weight of this polymer is preferably from 50,000 to 100,000. This polymer is sold under the trademark "Yukaformer" or "Diaformer" supplied by Mitsubishi Chemical Corporation.

(2) Useful herein are the betainized polymers containing zwitterionic units derived form the formula:



wherein R<sup>1</sup> denotes a polymerisable unsaturated group, such as an acrylate, methacrylate, acrylamide or methacrylamide group, x and y independently represent an integer from 1 to 3, R<sup>2</sup> and R<sup>3</sup> independently represent hydrogen, methyl, ethyl or propyl, and R<sup>4</sup> and R<sup>5</sup> independently represent a hydrogen atom or an alkyl radical such that the sum of the carbon atoms in R<sup>4</sup> and R<sup>5</sup> does not exceed 10.

Highly preferred betainized amphoteric polymers include commercially available material such as YUKAFORMER SM, YUKAFORMER FH, YUKAFORMER 301, YUKAFORMER 204WL, YUKAFORMER 510, YUKAFORMER M-75, YUKAFORMER R250S, Diaformer Z-SM, and Diaformer Z-W supplied by Mitsubishi Chemical Corporation.

#### Non-betainized Amphoteric Fixative Polymers

(3) Useful herein are the non-betainized amphoteric polymers resulting from the copolymerisation of a vinyl monomer carrying at least one carboxyl group, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, crotonic acid, or alphachloroacrylic acid, and a basic monomer which is a

substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl methacrylates and acrylates and dialkylaminoalkylmethacrylamides and -acrylamides.

5 (4) Useful herein are the non-betainized amphoteric polymers containing units derived from

- i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,
- ii) at least one acid comonomer containing one or more reactive carboxyl groups, and
- 10 iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quarternary ammonium substituents, of acrylic and methacrylic acids, and the product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

15 The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen 20 more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

25 Highly preferred non-betainized amphoteric polymers include commercially available material such as octylacrylamine/acrylates/butylaminoethyl methacrylate copolymers with the tradenames AMPHOMER, AMPHOMER SH701, AMPHOMER 28-4910, AMPHOMER LV71, and AMPHOMER LV47 supplied by National Starch & Chemical.

#### Cationic Fixative Polymer

The cationic fixative polymers useful herein are:

- (1) Vinylpyrrolidone / quaternized dialkylaminoalkyl acrylate or methacrylate copolymers such as those sold under the tradename Gafquat 734 and 35 755N by the Gaf Corp.

- (2) Cellulose ether derivatives containing quaternary ammonium groups.  
(3) Cationic polysaccharides.  
(4) Cationic polymers chosen from the group comprising:  
i) polymers containing units of the formula:

5 -A-Z<sup>1</sup>-A-Z<sup>2</sup>- (I)

wherein A denotes a radical containing two amino groups, preferably a piperazinyl radical, and Z<sup>1</sup> and Z<sup>2</sup> independently denote a divalent radical which is a straight-chain or branched-chain alkylene radical which contains up to about 7 carbon atoms in the main chain, is unsubstituted or substituted by one or more hydroxyl groups and can also contain one or more oxygen, nitrogen and sulphur atoms and 1 to 3 aromatic and/or heterocyclic rings, the oxygen, nitrogen and sulphur atoms generally being present in the form of an ether or thioether, sulphoxide, sulphone, sulphonium, amine, alkylamine, alkenylamine, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester and/or urethane group:

**ii) polymers containing units of the formula:**

-A-Z'-A-Z'- (II)

wherein A denotes a radical containing two amino groups, preferably a piperazinyl radical, and Z' denotes the symbol Z<sup>3</sup> and Z<sup>4</sup> while denoting the symbol Z<sup>4</sup> at least once; Z<sup>3</sup> denotes a divalent radical which is a straight-chain or branched-chain alkylene or hydroxyalkylene radical having up to about 7 carbon atoms in the main chain, and Z<sup>4</sup> is a divalent radical which is a straight-chain or branched-chain alkylene radical which has up to about 7 carbon atoms in the main chain, is unsubstituted and substituted by one or more hydroxyl radicals and is interrupted by one or more nitrogen atoms, the nitrogen atom being substituted by an alkyl chain having from 1 to 4 carbon atoms, preferably 4 carbon atoms, which is optionally interrupted by an oxygen atom and optionally contains one or more hydroxyl groups; and

30                   iii) the alkylation products, with alkyl and benzyl halides of 1 to 6 carbon atoms, alkyl tosylates or mesylates, and the oxidation products, of the polymers of the formulae (I) and (II) indicated above under i) and ii).

(5) Polyamino-polyamides prepared by the polycondensation of an acid compound with a polyamine. The acid compound can be organic dicarboxylic acids, aliphatic monocarboxylic and dicarboxylic acids containing a double bond, esters of the abovementioned acids, preferably

the esters with lower alkanols having from 1 to 6 carbon atoms, and mixtures thereof. The polyamine is a bis-primary or mono- or bis-secondary polyalkylene-polyamine wherein up to 40 mol% of this polyamine can be a bis-primary amine, preferably ethylenediamine, or a bis-secondary amine, preferably piperazine, and up to 20 mol% can be hexamethylenediamine.

- (6) The above mentioned polyamino-polyamides can be alkylated and/or crosslinked. The alkylation can be carried out with glycidol, ethylene oxide, propylene oxide or acrylamide. The crosslinking is carried out by means of a crosslinking agent such as:

  - i) epihalogenohydrins, diepoxides, dianhydrides, unsaturated anhydrides and bis-saturated derivatives, in proportions of 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino-polyamide;
  - ii) bis-halogenohydrins, bis-azetidinium compounds, bishalogeno acyldiamines and bis-(alkyl halides);
  - iii) oligomers obtained by reacting a compound chosen from the group comprising bis-halogenohydrins, bis-azetidinium compounds, bis-halogenoacyl-diamines, bis-(alkyl halides), epihalogenohydrins, diepoxides and bis-unsaturated derivatives, with another compound which is a difunctional compound which is reactive towards the compound; and
  - iv) the quaternisation product of a compound chosen from the compounds ii) and the oligomers iii) and containing one or more tertiary amine groups which can be totally or partially alkylated with an alkylating agent preferably chosen from methyl or ethyl chlorides, bromides, iodides, sulphates, mesylates and tosylates, benzyl chloride or bromide, ethylene oxide, propylene oxide and glycidol, the crosslinking being carried out by means of 0.025 to 0.35 mol, in particular of 0.025 to 0.2 mol and more particularly of 0.025 to 0.1 mol, of crosslinking agent per amine group of the polyamino-polyamide.

(7) Polyamino-polyamide derivatives resulting from the condensation of a polyalkylene-polyamine with a polycarboxylic acid, followed by alkylation by means of difunctional agents, such as the adipic acid/dialkylaminohydroxyalkyl-dialkylenetriamine copolymers in which the alkyl radical contains 1 to 4 carbon atoms and preferably denotes methyl,

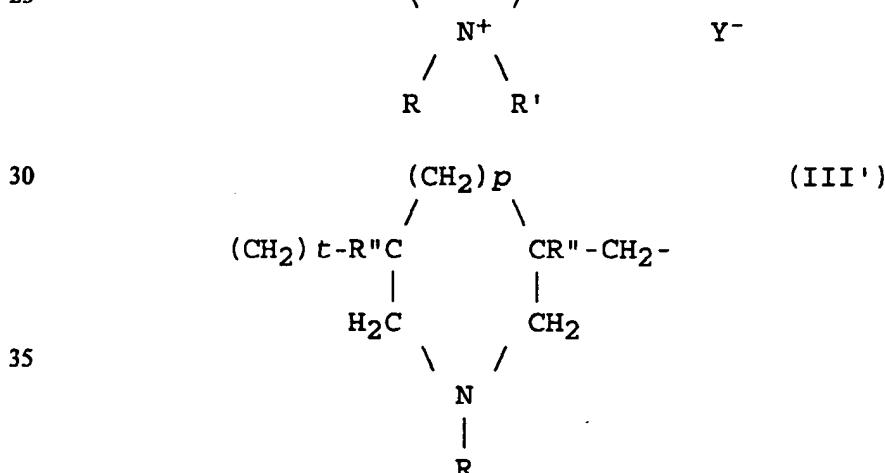
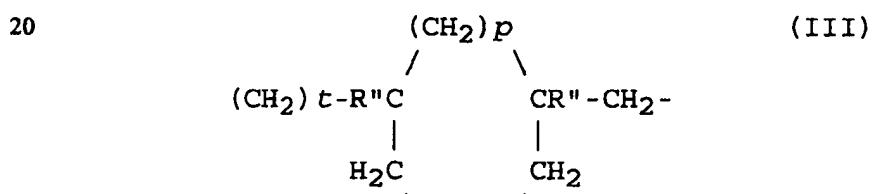
ethyl or propyl.

Useful polymers are adipic acid/dimethylaminohydroxypropyl-diethylenetriamine copolymers sold under the name Cartareline F, F<sup>4</sup> or F<sup>8</sup> by SANDOZ.

- 5 (8) Polymers obtained by reacting polyalkylenepolyamine containing two primary amine groups and at least one secondary amine group, with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids having 3 to 8 carbon atoms, the molar ratio of the polyalkylene-polyamine to the dicarboxylic acid being from 0.8:1 to 1.4:1,  
10 and the resulting polyamide being reacted with epichlorohydrin in a molar ratio of epichlorohydrin to the secondary amine groups of the polyamide of from 0.5:1 to 1.8:1.

Useful polymers are those sold under the name HERCOSETT 57 by Hercules Incorporated, and that sold under the name PD 170 or DELSETTE 101 by Hercules.

- (9) Cyclic polymers generally having a molecular weight of 20,000 to 3,000,000 such as homopolymers containing, as the main constituent of the chain, units corresponding to the formula (III) or (III')

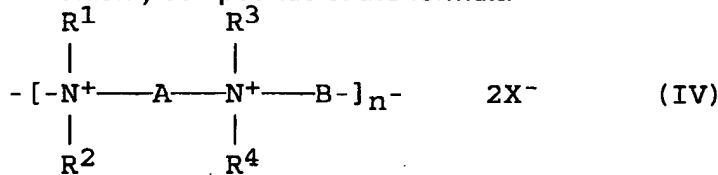


in which p and t are 0 or 1, and p+t=1, R" denotes hydrogen or methyl, R and R'

independently of one another denote an alkyl group having from 1 to 22 carbon atoms, a hydroxylalkyl group in which the alkyl group preferably has 1 to 5 carbon atoms, or a lower amidoalkyl group, and R and R' can denote, together with the nitrogen atom to which they are attached, heterocyclic groups such as 5 piperidinyl or morpholinyl, and Y is bromide, chloride, acetate, borate, citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate. Copolymers containing units of the formula III and III' may also contain units derived from acrylamide or from diacetoneacrylamide.

Amongst the quaternary ammonium polymers of the type defined above, 10 those which are preferred are the dimethyldiallylammmonium chloride homopolymer sold under the name MERQUAT 100 and having a molecular weight of less than 100,000, and the dimethyldiallylammmonium chloride/acrylamide copolymer having a molecular weight of more than 500,000 and sold under the name MERQUAT 550 by CALGON Corporation.

15 (10) Poly-(quaternary ammonium) compounds of the formula

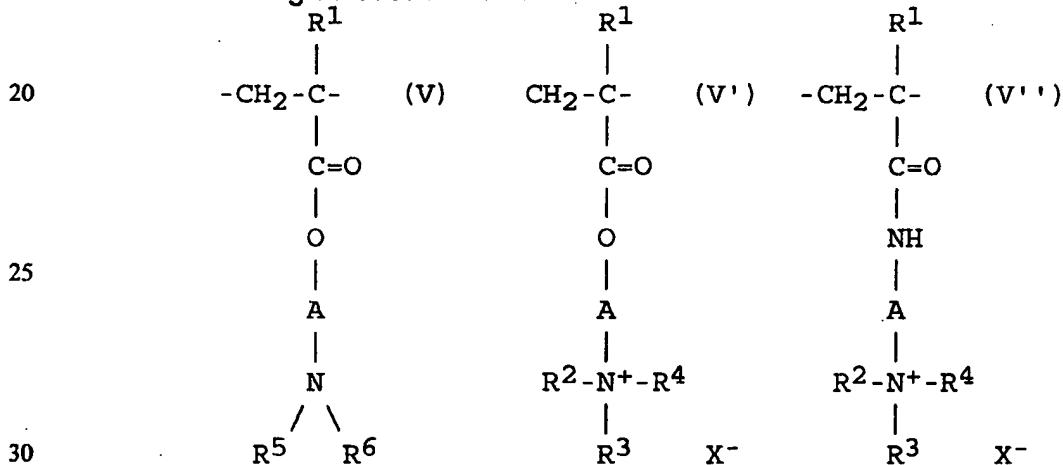


wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently aliphatic, alicyclic or arylaliphatic radicals containing a maximum of 20 carbon atoms, or lower hydroxylaliphatic radicals, or alternatively, with the nitrogen atoms to which they are attached, heterocyclic rings optionally containing a second hetero-atom other than 20 nitrogen, or alternatively R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> represent a group CH<sub>2</sub>CHR'<sup>3</sup>R'<sup>4</sup> wherein R'<sup>3</sup> denoting hydrogen or lower alkyl and R'<sup>4</sup> denoting SO, CN, CON(R'<sup>6</sup>)<sub>2</sub>, COOR'<sup>5</sup>, COR'<sup>5</sup>, COOR'<sup>7</sup>D, or CONHR'<sup>7</sup>D; R'<sup>5</sup> denoting lower alkyl, R'<sup>6</sup> denoting hydrogen or lower alkyl, R'<sup>7</sup> denoting alkylene and D denoting a quaternary ammonium group; A and B independently represent a polymethylene group containing from 2 to 20 carbon atoms, which can be linear or branched, saturated or unsaturated and can contain, inserted in the main chain one or more groups -CH<sub>2</sub>-Y-CH<sub>2</sub>- wherein Y denotes benzene, oxygen, sulfur, SO, SO<sub>2</sub>, SS, NR'<sup>8</sup>, N<sup>+(R'<sup>9</sup>)<sub>2</sub>X<sup>1-</sup></sup>, CHO, NHCONH, CONR'<sup>8</sup>, or COO; X<sup>1-</sup> denoting an anion derived from a mineral or organic acid, R'<sup>8</sup> denoting hydrogen or lower alkyl and R'<sup>9</sup> denoting lower alkyl, or alternatively A and R<sup>1</sup> and R<sup>3</sup> form a piperazine ring with the two nitrogen atoms to which they are attached. If A denotes a linear or

branched, saturated or unsaturated alkylene or hydroxyalkylene radical, B can also denote a group:  $-(CH_2)_n-CO-D-OC-(CH_2)_n-$ ; wherein n is selected so that the molecular weight is generally between 1,000 and 100,000; and D denotes:

- 5      i) a glycol radical of the formula  $-O-Z-O-$ , in which Z denotes a linear or branched hydrocarbon radical or a group corresponding to the formulae:  
 $-[CH_2-CH_2-O]_x-CH_2-CH_2-$  or  $-[CH_2-C(CH_3)H-O]_y-CH_2-C(CH_3)H-$   
 wherein x and y denote an integer from 1 to 4, representing a definite and unique degree of polymerisation;
- 10     ii) a bis-secondary diamine radical, such as a piperazine derivative;
- iii) a bis-primary diamine radical of the formula:  $-N-H-Y-NH-$ , in which Y denotes a linear or branched hydrocarbon radical or the divalent radical  
 $-CH_2-CH_2-S-S-CH_2-CH_2-$ ; or
- 15     iv) a ureylene group of the formula  $-N-H-CO-NH-$ .

- (11) Homopolymers or copolymers derived from acrylic or methacrylic acid and containing at least one unit:



wherein  $R^1$  is H or  $CH_3$ , A is a linear or branched alkyl group having 1 to 6 carbon atoms or a hydroxyalkyl group having 1 to 4 carbon atoms,  $R^2$ ,  $R^3$  and  $R^4$  independently denote an alkyl group having 1 to 18 carbon atoms or a benzyl group,  $R^5$  and  $R^6$  denote H or alkyl having 1 to 6 carbon atoms and X denotes methosulphate or halide, such as chloride or bromide.

The comonomer or comonomers which can be used typically belong to the family comprising: acrylamide, methacrylamide, diacetone-acrylamide, acrylamide and methacrylamide substituted on the nitrogen by one or more low

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alkyls, alkyl esters of acrylic and methacrylic acids, vinylpyrrolidone and vinyl esters.

- Useful polymers are Quaternium 38, 37, 49 and 42 in the CTFA, acrylamide/beta-methacryloyloxyethyl-trime-thylammonium methosulphate 5 copolymers sold under the names Teten 205,210,220 and 240 by Hercules, and aminoethylacrylate phosphate/acrylate copolymer sold under the name Catrex by National Starch & Chemicals, and the crosslinked graft cationic copolymers having a molecular weight of 10,000 to 1,000,000, and preferably of 15,000 to 10 500,000, and resulting from the copolymerisation of: at least one cosmetic monomer, dimethylaminoethyl methacrylate, polyethylene glycol and a polyunsaturated crosslinking agent, such as those mentioned in the CTFA 15 dictionary under the name AMODIMETHICONE, such as the product marketed as a mixture with other ingredients under the name DOW CORNING 929 cationic emulsion.
- 15 (12) Other cationic polymers which can be used are polyalkyleneimines, in particular polyethyleneimines, polymers containing vinylpyridine units or vinylpyridinium units in the chain, condensates of polyamines and of epichlorohydrin, poly-(quaternary ureylenes) and chitin derivatives.

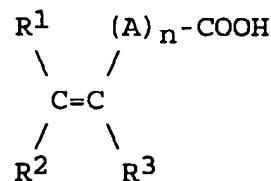
Highly preferred cationic fixative polymers include commercially available 20 material such as Polyquaternium 4 under the tradenames CELQUAT H100 and CELQUAT L200 supplied by National Starch & Chemicals, and Polyquaternium 11 under the tradename GAFQUAT 755N supplied by ISP.

#### Anionic Fixative Polymer

The anionic fixative polymers useful herein include polymers containing 25 units derived from carboxylic, sulphonic or phosphoric acid and usually have a molecular weight of 500 to 5,000,000. These polymers are water-soluble polymers, it being possible for this solubility to be obtained by neutralisation.

The carboxylic acid groups can be provided by unsaturated 30 monocarboxylic or dicarboxylic acids, such as those corresponding to the formula:

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wherein n is 0 or an integer from 1 to 10, A denotes a methylene group optionally joined to the carbon atom of the saturated group, or to the adjacent methylene group in the case where n is greater than 1, via a heteroatom, such as oxygen or sulphur, R<sup>1</sup> denotes a hydrogen atom or a phenyl or benzyl group, R<sup>2</sup> denotes a hydrogen atom, a lower alkyl group or a carboxyl group and R<sup>3</sup> denotes a hydrogen atom, a lower alkyl group, CH<sub>2</sub>COOH, or a phenyl or benzyl group.

According to the invention, the preferred polymers containing carboxylic acid groups are:

- 10 (1) Homopolymers or copolymers of acrylic or methacrylic acid or salts thereof, and in particular, the products sold under the name VERSICOL E or K, and ULTRAHOLD by BASF and under the name DARVAN No. 7 by Van der Bilt; acrylic acid/acrylamide copolymers sold in the form of their sodium salt under the name RETEN 421, 423 or 425 by HERCULES; and the sodium salts of polyhydroxycarboxylic acids, sold under the name HYDAGEN F by HENKEL.
- 15 (2) Copolymers of acrylic or methacrylic acid with a monoethylenic monomer, such as ethylene, styrene, a vinyl or allyl ester or acrylic or methacrylic acid ester, optionally grafted onto a polyalkylene glycol, such as polyethylene glycol, and optionally crosslinked. Other such copolymers contain an optionally N-alkylated and/or N-hydroxylated acrylamide unit in their chain, such as those sold under the name QUADRAMER 5 by American Cyanamid.
- 20 (3) Copolymers derived from crotonic acid, such as those containing, in their chain, vinyl acetate or propionate units and optionally other monomers such as allyl or methallyl esters, a vinyl ether or a vinyl ester of a saturated linear or branched carboxylic acid with a hydrocarbon chain of at least 5 carbon atoms, if appropriate, for these polymers to be grafted and crosslinked, or also a vinyl, allyl or methallyl ester of an α- or β-cyclic carboxylic acid. Included in this class are those with the tradename RESYN 28-2930, 28-2913, and 28-1310 sold by National Starch & Chemicals.
- 25 (4) Polymers derived from maleic, fumaric and itaconic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, such as those sold under the name GANTREZ A, SP,

and ES by ISP. Other polymers included in this class are copolymers of maleic, citraconic and itaconic anhydrides with an allyl or methallyl ester optionally containing an acrylamido or methacrylamido group, or with an  $\alpha$ -olefine, acrylic or methacrylic acid ester, acrylic or methacrylic acid or vinylpyrrolidone unit in their chain; the anhydride groups can be monoesterified or monoamidified.

- 5 (5) Polyacrylamides containing carboxylate groups. Polymers comprising sulphonic groups include polymers containing vinylsulphonic, styrenesulphonic, lignosulphonic or naphthalenesulphonic units. These polymers are chosen, in particular, from amongst:
- 10 i) Polyvinylsulphonic acid salts having a molecular weight of 1,000 to 100,000, and also copolymers with an unsaturated comonomer, such as acrylic or methacrylic acid or an ester thereof and also substituted or unsubstituted acrylamide or methacrylamide, vinyl esters, vinyl ethers and vinylpyrrolidone.
- 15 ii) Polystyrenesulphonic acid salts, such as the sodium salt sold by National Starch & Chemicals under the name Flexan 500 and 130.
- 20 iii) Alkali metal or alkaline earth metal salts of sulphonic acids derived from lignin, and more particularly calcium lignosulphonates or sodium lignosulphonates, such as the product sold under the name Marasperse C-21 by American Can Co. and the C<sub>10</sub> to C<sub>14</sub> products sold by Avebene.
- 25 iv) Polymers containing salfied alkynaphthalenesulphonic acid units, such as the sodium salt under the name Darvan No. 1 by Van der Bilt.
- The anionic hair fixative polymers herein which include anionic monomers are preferably utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. In the compositions the neutralisation of a polymer may be achieved by use of an inorganic base, preferably KOH. However organic base, preferably AMP (amino methyl propanol) and mixture of inorganic and organic base may also be used to effect the desired level of neutralisation in hair styling compositions. In total from about 50% to about 100%, preferably from about 70% to about 100%, most preferably from about 80% to about 100% of the acidic monomers of each polymer utilised should be neutralised with base.
- 30 35 Any conventionally used base, organic or inorganic, may be used for

neutralisation of acidic polymers provided they are utilised as specified herein. Hydroxides of alkali, alkaline earth and amino alcohols are suitable neutralisers.

Examples of suitable organic neutralizing agents which may be included in the compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1, 3-propanediol (AMPD), 2-amino-2ethyl-1, 3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine (TIPA), dimethylsteramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

Preferred neutralising agents for use in hair treating compositions of the present invention are potassium and sodium hydroxides.

Highly preferred anionic fixative polymers include commercially available material such as vinyl acetate/crotonic acid/vinyl neodecanoate copolymers and vinyl acetate/crotonic acid copolymers with the tradenames RESYN 28-2930, RESYN 28-2913, and RESYN 28-1310 supplied by National Starch & Chemicals, and acrylates copolymers and acrylates/acrylamide copolymers with tradenames LUVIMER 100P, ULTRAHOLD 8, and ULTRAHOLD STRONG supplied by BASF Corporation.

## 20 Nonionic Fixative Polymers

Nonionic fixative polymers useful herein are homopolymer of vinylpyrrolidone or vinylcaprolactum and copolymers of vinylpyrrolidone with vinylacetate such as those with tradenames LUVISKOL K grades and LUVISKOL VA grades supplied by BASF Corporation.

## 25 II. Optional Ingredients for Hair Treating Compositions

Such optional ingredients may include, for example, anti-dandruff actives such as zinc pyrithione, octopirox, selenium disulfide, sulfur, coal tar, and the like, preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; cationic conditioning agents, including both cationic 30 conditioning surfactants and cationic conditioning polymers; quaternary polymeric foam boosters, such as Polyquaternium 10, preferably from about 0.01% to about 0.2%, by weight of the composition; fatty alcohols; block polymers of ethylene oxide and propylene oxide such as Pluronic F88 offered by BASF Wyandotte; sodium chloride, sodium sulfate; ammonium xylene sulfonate; 35 propylene glycol; polyvinyl alcohol; ethyl alcohol; pH adjusting agents such as

citric acid, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate, etc.; perfumes; and dyes. These optional ingredients are typically used at levels of from about 0.01% to about 10% of the composition.

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(iv) Antiperspirant and/or Deodorant Compositions

The antiperspirant and/or deodorant compositions of the present invention generally includes: from about 0.002% to about 1% of a malodor reducing composition of the present invention; from about 0.01% to about 95% of a surfactant system; and the balance comprising water, wherein the total amount 10 of the amber chemical material and the musk material (1) in the malodor reducing composition is at least about 5% by weight; and (2) in the antiperspirant and/or deodorant compositions is from about 0.0001% to about 1%.

I. Optional Ingredients for Antiperspirant and/or Deodorant Compositions

Some antiperspirant gel stick compositions of the present invention may 15 include the ingredients discussed below. Although the term "stick" as utilized herein includes semi-solid forms (i.e., preferably having a viscosity of at least about 1,000,000 centipoise at 25°C), solid forms (i.e., preferably having an average penetration value within a given production batch from about 3 to about 25 mm over a period of 5 seconds as measured utilizing American Society for 20 Testing Materials (ASTM) Method D-5, with a penetration cone (Model H1312; sold by Humbolt Manufacturing Company) weighing 2.0 g (making the total mass 50 g and a Sommer & Runge Model PNR10 Penetrometer) are preferred.

Gelling Agent:

The "gelling agent" as used herein is a mixture of a primary gellant and a 25 secondary gellant; both discussed hereinafter. The primary gellant is selected from the group consisting of 12-hydroxystearic acid, esters of 12-hydroxystearic acid, amides of 12-hydroxystearic acid and mixtures thereof. The secondary gellant is selected from the group consisting of n-acyl amino acid derivatives. The level of the gelling agent within the composition is typically from about 1% to 30 about 15%; preferably, from about 3% to about 12%; more preferably, from about 5% to about 10%. The primary gellant:secondary gellant ratio is typically between about 1:2 and about 20:1; preferably, from about 1:1 to about 10:1; more preferably, from about 2:1 to about 7:1; and even more preferably, from about 3:1 to about 5:1. The primary gellant:secondary gellant ratio appears to be more critical when the level of polar, non-volatile liquid within the liquid base material 35

(discussed hereinafter) in the composition is relatively low; e.g., below about 25%.

This gelling agent offers significant benefits when used in an antiperspirant gel stick. The gelling agent of the present invention exhibits unexpected benefits, 5 e.g., decreased residue upon application to the skin, increased hardness and better aesthetics, relative to a similar composition having either of the two gellants alone. In fact, these gellants in combination are more effective than either alone so that the overall level of gelling agent within the composition can be reduced while maintaining such desirable stick characteristics.

10 Moreover, when these gellants are used together as the gelling agent of the present invention, degradation of the gelling agent by the acidic antiperspirant active during manufacturing is unexpectedly significantly reduced; i.e., as compared to each gellant alone. To further reduce degredation, a heated solution of the gelling agent and the liquid base material preferably remains in 15 solution such that the antiperspirant active can be substantially uniformly mixed therein at a temperature less than about 120°C; more preferably, less than about 105°C; more preferably, less than about 95°C; and most preferably, less than about 80°C (hereinafter, the "mixing temperature"). This reduced mixing temperature is made possible partly because the primary gellant, once molten, is 20 an unexpectedly good co-solvent for the secondary gellant, thereby facilitating their dissolution at a lower temperature. Additional methods of reducing the mixing temperature or otherwise enabling a reduction of the interaction of the acidic antiperspirant active with other components, e.g., the gelling agent, is discussed hereinafter. Since lower mixing temperatures can be utilized, the 25 gelling agent is more compatible with additional gel stick components which have lower boiling points, such as perfumes.

a. Primary Gellant

The primary gellant of the gelling agent of the present invention is selected from the group consisting of 12-hydroxystearic acid, esters of 12-hydroxystearic 30 acid, amides of 12-hydroxystearic acid and mixtures thereof. The primary gellant is preferably selected from the group consisting of 12-hydroxystearic acid, 12-hydroxystearic acid methyl ester, 12-hydroxystearic acid ethyl ester, 12-hydroxystearic acid stearyl ester, 12-hydroxystearic acid benzyl ester, 12-hydroxystearic acid amide, isopropyl amide of 12-hydroxystearic acid, butyl amide 35 of 12-hydroxystearic acid, benzyl amide of 12-hydroxystearic acid, ph nyl amide

of 12-hydroxystearic acid, t-butyl amide of 12-hydroxystearic acid, cyclohexyl amide of 12-hydroxystearic acid, 1-adamantyl amide of 12-hydroxystearic acid, 2-adamantyl amide of 12-hydroxystearic acid, diisopropyl amide of 12-hydroxystearic acid, and mixtures thereof; even more preferably, 12-hydroxystearic acid, isopropyl amide of 12-hydroxystearic acid, and mixtures thereof.

5        b. Secondary Gellant

With regard to the secondary gellant of the gelling agent of the present invention, N-acyl amino acid derivatives include N-acyl amino acid amides and N-acyl amino acid esters prepared from glutamic acid, lysine, glutamine, aspartic acid and mixtures thereof.

10      Preferably the N-acyl amino acid derivatives are selected from the group consisting of N-lauroyl-glutamic acid diethyl amide, N-lauroyl-glutamic acid dibutyl amide, N-lauroyl-glutamic acid dihexyl amide, N-lauroyl-glutamic acid dioctyl amide, N-lauroyl-glutamic acid didecyl amide, N-lauroyl-glutamic acid didodecyl amide, N-lauroyl-glutamic acid ditetradecyl amide, N-lauroyl-glutamic acid dihexadecyl amide, N-lauroyl-glutamic acid distearyl amide, N-stearoyl-glutamic acid dibutyl amide, N-stearoyl-glutamic acid dihexyl amide, N-stearoyl-glutamic acid diheptyl amide, N-stearoyl-glutamic acid dioctyl amide, N-stearoyl-glutamic acid didecyl amide, N-stearoyl-glutamic acid didodecyl amide, N-stearoyl-glutamic acid ditetradecyl amide, N-stearoyl-glutamic acid dihexadecyl amide, N-stearoyl-glutamic acid distearyl amide and mixtures thereof; more preferred, is n-lauroyl-glutamic acid dibutyl amide, n-stearyl-glutamic acid dihexyl amide, and mixtures thereof.

15      25     Liquid Base Materials

The liquid base matrix of antiperspirant stick compositions of the present invention is formed by combining the gelling agent with a liquid base material. As used herein, the term "liquid" refers to materials which are liquids at ambient conditions and the term "liquid base material" includes all liquids within the composition. It is important that the liquid base material be of a type, and used at a level sufficient to solubilize the gelling agent when heated, to permit substantially uniform mixing of the antiperspirant active into the heated solution at the mixing temperature, and form a stick when cooled to ambient temperature. The liquid base material should be compatible with the gelling agent so that the mixture of the two remains homogeneous and does not phase separate during

manufacturing and so that the finished product remains homogeneous and does not phase separate at ambient conditions over the normal shelf-life which may be upwards of one year. Furthermore, the liquid base materials are typically selected to provide aesthetic benefits, such as emolliency, low tack or minimized visible residue, without significant interference with the effectiveness of the antiperspirant active component. Lastly, the particular liquid base material should be safe for application to human skin.

The liquid base materials include emollients which have a solubility parameter from about 5 to about 11. It is preferable that, in aggregate, the average solubility parameter of the liquid base material be from about 6 to about 10. Hence, a mixture of emollients may be used as the liquid base material herein, each having a solubility parameter in the range of from about 5 to about 11, such that the average solubility parameter of the mixture is from about 6 to about 10. Solubility parameters are common to the art of antiperspirant stick formulation and the means to determine them are disclosed by C.D. Vaughan, "Solubility Effects in Product, Package, Penetration and Preservation" 103 Cosmetics and Toiletries 47-69, October, 1988; and C.D. Vaughan, "Using Solubility Parameters in Cosmetics Formulation", 36 J Soc. Cosmetic Chemists 319-333, Sept/Oct, 1985.

The liquid base material of the present invention is preferably used at levels from about 10% to about 95%; and more preferably from about 45% to about 80%. The liquid base material preferably includes a volatile, non-polar, oil and a non-volatile, relatively polar co-solvent; each discussed more fully hereinafter. The term "non-volatile" as used herein refers to materials which exhibit a vapor pressure of no more than about 0.2mm Hg at 25°C at one atmosphere and/or to materials which have a boiling point at one atmosphere of at least about 300°C. The term "volatile" as used herein refers to all materials which are not "non-volatile" as previously defined herein. The phrase "relatively polar" as used herein means more polar than another material in terms of solubility parameter; i.e., the higher the solubility parameter the more polar the liquid. The term "non-polar" typically means that the emollient has a solubility parameter below about 6.5.

a. Non-polar, Volatile Oil

The non-polar, volatile oil tends to impart highly desirable aesthetic properties to the gel stick. Consequently, the non-polar, volatile oils are

preferably utilized at a fairly high level. Such non-polar, volatile oils are preferably used at levels from about 10% to about 70%; more preferably, from about 25% to about 60%; more preferably from about 40% to about 60%.

Non-polar, volatile oils particularly useful in the present invention are selected from the group consisting of silicone oils; hydrocarbons; and mixtures thereof. Such non-polar, volatile oils are disclosed, for example, in *Cosmetics, Science, and Technology*, Vol. 1, 27-104 edited by Balsam and Sagarin, 1972. The non-polar, volatile oils useful in the present invention may be either saturated or unsaturated, have an aliphatic character and be straight or branched chained or contain alicyclic or aromatic rings. Examples of preferred non-polar, volatile hydrocarbons include isodecane (such as *Permethyl-99A®* which is available from Presperse Inc.) and the C<sub>7</sub>-C<sub>8</sub> through C<sub>12</sub>-C<sub>15</sub> isoparaffins (such as the *Isopar® Series* available from Exxon Chemicals).

Non-polar, volatile silicone oils are highly preferred as the non-polar, volatile oil in the liquid base material, since they endow the antiperspirant stick composition with highly desirable aesthetics. Non-polar, volatile liquid silicone oils are disclosed in U.S. Pat. 4,781,917 issued to Luebbe et al. on Nov. 1, 1988. Additionally, a description of various volatile silicones materials is found in Todd et al., "Volatile Silicone Fluids for Cosmetics", *Cosmetics and Toiletries*, 91:27-32 (1976). Particularly preferred volatile silicone oils are cyclic and linear volatile silicones like those disclosed hereinbefore.

b. Relatively Polar, Non-volatile Co-solvent

The relatively polar co-solvent aids in the utilization of reduced processing temperatures by solubilizing at least one of the gellants and being soluble in the non-polar, volatile oil when subjected to reduced processing temperatures. The non-volatile co-solvent is "relatively polar" as compared to the non-polar, volatile oil discussed above. Therefore, the non-volatile co-solvent is more polar (i.e., has a higher solubility parameter) than at least one of the non-polar, volatile oils.

In addition to enabling reduced processing temperatures, the co-solvent enables the inclusion of greater amounts of the non-polar, volatile oil. This is advantageous because, as discussed above, the non-polar, volatile oil provides significant cosmetic benefits. The quantity of relatively polar, non-volatile co-solvent, however, is preferably kept to a minimum because it tends to adversely affect product cosmetics. Thus, the relatively polar, non-volatile co-solvent is preferably included at levels from about 5% to about 60%; more preferably from

about 5% to about 25%; and most preferably from about 7% to about 20%.

- Relatively polar, non-volatile liquids potentially useful as the co-solvent in the present invention are disclosed, for example, in *Cosmetics, Science, and Technology*, Vol. 1, 27-104 edited by Balsam and Sagarin, 1972; U.S. Pat. 5 4,202,879 issued to Shelton on May 13, 1980; and U.S. Pat. 4,816,261 issued to Luebbe et al. on March 28, 1989. Relatively polar, non-volatile co-solvents useful in the present invention are preferably selected from the group consisting of silicone oils; hydrocarbon oils; fatty alcohols; fatty acids; esters of mono and dibasic carboxylic acids with mono and polyhydric alcohols; polyoxyethylenes; 10 polyoxypropylenes; mixtures of polyoxyethylene and polyoxypropylene ethers of fatty alcohols; and mixtures thereof. The relatively polar, non-volatile co-solvents useful in the present invention may be either saturated or unsaturated, have an aliphatic character and be straight or branched chained or contain alicyclic or aromatic rings.
- 15 More preferably, the relatively polar, non-volatile liquid co-solvent are selected from the group consisting of fatty alcohols having from about 12-26 carbon atoms; fatty acids having from about 12-26 carbon atoms; esters of monobasic carboxylic acids and alcohols having from about 14-30 carbon atoms; esters of dibasic carboxylic acids and alcohols having from about 10-30 carbon 20 atoms; esters of polyhydric alcohols and carboxylic acids having from about 5-26 carbon atoms; ethoxylated, propoxylated, and mixtures of ethoxylated and propoxylated ethers of fatty alcohols with from about 12-26 carbon atoms and a degree of ethoxylation and propoxylation of below about 50; and mixtures thereof.
- More preferred are propoxylated ethers of C<sub>14</sub>-C<sub>18</sub> fatty alcohols having a 25 degree of propoxylation below about 50, esters of C<sub>2</sub>-C<sub>8</sub> alcohols and C<sub>12</sub>-C<sub>26</sub> carboxylic acids (e.g. ethyl myristate, isopropyl palmitate), esters of C<sub>12</sub>-C<sub>26</sub> alcohols and benzoic acid (e.g. Finsolv TN® supplied by Finetex), diesters of C<sub>2</sub>-C<sub>8</sub> alcohols and adipic, sebacic, and phthalic acids (e.g., diisopropyl sebacate, 30 diisopropyl adipate, di-n-butyl phthalate), polyhydric alcohol esters of C<sub>6</sub>-C<sub>26</sub> carboxylic acids (e.g., propylene glycol dicaprate/dicaprylate, propylene glycol isostearate); and mixtures thereof.
- Even more preferred are branched-chain aliphatic fatty alcohols having from about 12-26 carbon atoms. Even more preferred is isocetyl alcohol, octyldecanol, octyldodecanol and undecylpentadecanol; and most preferred is 35 octyldodecanol. Such preferred aliphatic fatty alcohols are particularly useful in

combination with the volatile liquid silicone oils discussed herein to adjust the average solubility of the liquid base material.

c. Non-polar, Non-volatile Emollients

In addition to the liquids discussed above, the liquid base material can 5 optionally include non-volatile, non-polar emollients which tend to improve product cosmetics. Typical non-volatile, non-polar emollients are disclosed, for example, in *Cosmetics, Science, and Technology*, Vol. 1, 27-104 edited by Balsam and Sagarin, 1972; U.S. Pat. 4,202,879 issued to Shelton on May 13, 1980; and U.S. Pat. 4,816,261 issued to Luebbe et al. on March 28, 1989.get  
10 good dissolution. The non-volatile silicone oils useful in the present invention are essentially non-volatile polysiloxanes, paraffinic hydrocarbon oils, and mixtures thereof. The polysiloxanes useful in the present invention selected from the group consisting of polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, poly-ethersiloxane copolymers, and mixtures thereof. Examples of these include  
15 polydimethyl siloxanes having viscosities of from about 5 to about 100,000 centistokes at 25°C.

Among the preferred non-volatile silicone emollients useful in the present compositions are the polydimethyl siloxanes having viscosities from about 2 to about 400 centistokes at 25°C. Such polyalkylsiloxanes include the Viscasil® 20 series (sold by General Electric Company) and the Dow Corning 200 series (sold by Dow Corning Corp.). Polyalkylarylsiloxanes include polymethylphenyl siloxanes having viscosities of from about 15 to about 65 centistokes at 25°C. These are available, for example, as SF 1075 methyl-phenyl fluid (sold by General Electric Company) and 556 Cosmetic Grade Fluid (sold by Dow Corning 25 Corp.). Useful poly-ethersiloxane copolymers include, for example, a polyoxyalkylene ether copolymer having a viscosity of about 1200 to 1500 centistokes at 25°C. Such a fluid is available as SF1066 organosilicone surfactant (sold by General Electric Company). Polysiloxane ethylene glycol ether copolymers are preferred copolymers for use in the present compositions.

30 Non-volatile paraffinic hydrocarbon oils useful in the present invention include mineral oils and certain branched-chain hydrocarbons. Examples of these fluids are disclosed in U.S. Pat. 5,019,375 issued to Tanner et al. on May 28, 1991. Preferred mineral oils have the following properties:

- 35 (1) viscosity from about 5 centistokes to about 70 centistokes at 40°C;  
(2) density between about 0.82 and 0.89 g/cm<sup>3</sup> at 25°C;

- (3) flash point between about 138°C and about 216°C; and
- (4) carbon chain length between about 14 and about 40 carbon atoms.

Preferred branched chain hydrocarbon oils have the following properties:

- 5 (1) density between about 0.79 and about 0.89 g/cm<sup>3</sup> at 20°C
- (2) boiling point greater than about 250°C; and
- (3) flash point between about 110°C and about 200°C.

Particularly preferred branched-chain hydrocarbons include Permethyl 103A, which contains an average of about 24 carbon atoms; Permethyl 104A, which contains an average of about 68 carbon atoms; Permethyl 102A, which contains 10 an average of about 20 carbon atoms; all of which may be purchased from Permethyl Corporation; and Ethylflo 364 which contains a mixture of 30 carbon atoms and 40 carbon atoms and may be purchased from Ethyl Corp.

Additional components useful in formulating these topical compositions are further described below.

15 II Additional Components for Hair Treating Compositions, Antiperspirant and/or Deodorant Compositions

A wide variety of additional components can be employed in the hair treating compositions, antiperspirant and/or deodorant compositions herein.

Non-limiting examples include the following:

20 1. Deodorant Active Ingredients

Suitable types of deodorant actives include antimicrobial ingredients such as bactericides and fungicides. Exemplary deodorant actives include quaternary ammonium compounds such as cetyl-trimethylammonium bromide, cetyl pyridinium chloride, benzethonium chloride, diisobutyl phenoxy ethoxy ethyl 25 dimethyl benzyl ammonium chloride, sodium N-lauryl sarcosine, sodium N-palmethyl sarcosine, lauroyl sarcosine, N-myristoyl glycine, potassium N-lauryl sarcosine, stearyl, trimethyl ammonium chloride, sodium aluminum chlorohydroxy lactate, tricetyl methyl ammonium chloride, 2,4,4'-trichlorio-2'-hydroxy diphenyl ether, diaminoalkyl amides such as L-lysine hexadecyl amide, heavy metal salts 30 of citrate, salicylate, and piroctose, especially zinc salts, and acids thereof, heavy metal salts of pyrithione, especially zinc pyrithione and zinc phenolsulfate. Still other antimicrobial ingredients include farnesol.

Other deodorant actives include odor absorbing materials such as carbonate and bicarbonate salts, e.g. as the alkali metal carbonates and 35 bicarbonates, ammonium and trialkylammonium carbonates and bicarbonates,

especially the sodium and potassium salts.

Mixtures of deodorant actives are also contemplated and intended to be encompassed herein.

## 2. Antiperspirant Actives

5 The compositions of the present invention can also contain an astringent antiperspirant active. These actives are typically used at levels from about 0.5% to about 60%, preferably from about 5% to about 35%, in, e.g., an antiperspirant gel stick composition. This active can be incorporated either in solubilized or particulate form. These weight percentages are calculated on an anhydrous  
10 metal salt basis (exclusive of, e.g., glycine, the salts of glycine, or other complexing agents). Such materials include, for example, many aluminum or zirconium astringent salts or complexes and are well known in the antiperspirant art.

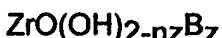
15 The antiperspirant active is preferably in particulate form wherein the surface area of the active is relatively low. The surface area of the antiperspirant active can be reduced by increasing the size and density of the active particles. Consequently, the particulate antiperspirant active preferably has a density which is preferably greater than about 0.7 g/cm<sup>3</sup> and an average particle size (as measured by a Coulter Multisizer 11 manufactured by Coulter Corporation,  
20 Haleah, Florida) greater than about 10 microns; more preferably, greater than about 30 microns; and most preferably, greater than about 40 microns. Such preferred materials can be purchased from Westwood Chemical Company, Middletown, N.Y. under the trade name Westchlor® ZR. Suitable antiperspirant active is disclosed, for example in U.S. Patent 4,147,766 which issued on April 3,  
25 1979 to Kozischek.

Any aluminum astringent antiperspirant salt or aluminum and/or zirconium astringent complex can be employed herein. Salts useful as astringent antiperspirant salts or as components of astringent complexes include aluminum halides, aluminum hydroxy-halides, zirconyl oxyhalides, zirconyl hydroxy-halides, and mixtures of these materials.  
30

Aluminum salts of this type include aluminum chloride and the aluminum hydroxyhalides having the general formula  $\text{Al}_2(\text{OH})_x\text{Q}_y\text{XH}_2\text{O}$  where Q is chlorine, bromine or iodine; where x is from about 2 to about 5, and x+y = about 6, and x and y do not need to be integers; and where X is from about 1 to about 35 6. Aluminum salts of this typ can be prepared in the manner described more

fully in U.S. Patent 3,887,692 issued to Gilman on June 3, 1975, and U.S. Patent 3,904,741 issued to Jones and Rubino on September 9, 1975.

The zirconium compounds which are useful in the present invention include both the zirconium oxy salts and zirconium hydroxy salts, also referred to 5 as the zirconyl salts and zirconyl hydroxy salts. These compounds may be represented by the following general empirical formula:



wherein z may vary from about 0.9 to about 2 and need not be an integer, n is 10 the valence of B, 2-nz is greater than or equal to 0, and B may be selected from the group consisting of halides, nitrate, sulfamate, sulfate, and mixtures thereof. Although only zirconium compounds are exemplified in this specification, it will be understood that other Group IVB metal compounds, including hafnium, can be used in the present invention.

As with the basic aluminum compounds, it will be understood that the 15 above formula is greatly simplified and is intended to represent and include compounds having coordinated and/or bound water in various quantities, as well as polymers, mixtures and complexes of the above. As will be seen from the above formula, the zirconium hydroxy salts actually represent a range of compounds having various amounts of the hydroxy group, varying from about 20 1.1 to only slightly greater than zero groups per molecule.

Several types of antiperspirant complexes utilizing the above 25 antiperspirant salts are known in the art. For example, U.S. Patent 3,792,068 issued to Luedders et al. on February 12, 1974 discloses complexes of aluminum, zirconium and amino acids, such as glycine. Complexes such as those disclosed in the Luedders et al. patent and other similar complexes are commonly known as ZAG. ZAG complexes are chemically analyzable for the presence of aluminum, zirconium and chlorine. ZAG complexes useful herein are identified by the specification of both the molar ratio of aluminum to zirconium (hereinafter "Al:Zr" ratio) and the molar ratio of total metal to chlorine 30 (hereinafter "Metal:Cl" ratio). ZAG complexes useful herein have an Al:Zr ratio of from about 1.67 to about 12.5 and a Metal:Cl ratio of from about 0.73 to about 1.93.

Preferred ZAG complexes are formed by

(A) co-dissolving in water

35 (1) on part  $\text{Al}_2(\text{OH})_{6-\text{m}}\text{Q}_m$ , wherein Q is an anion selected

from the group consisting of chloride, bromide and iodide, and m is a number from about 0.8 to about 2.0;

(2) x parts  $ZrO(OH)_{2-a}Q_a \cdot nH_2O$ , where Q is chloride, bromide or iodide; where a is from about 1 to about 2; where n is from about 1 to about 8; and where x has a value of from about 0.16 to about 1.2;

(3) p parts neutral amino acid selected from the group consisting of glycine, dl-tryptophane, dl-b-phenylalanine, dl-valine, dl-methionine and b-alanine, and where p has a value of from about 0.06 to about 0.53;

(B) co-drying the resultant mixture to a friable solid; and

(C) reducing the resultant dried inorganic-organic antiperspirant complex to particulate form.

A preferred aluminum compound for preparation of such ZAG type complexes is aluminum chlorhydroxide of the empirical formula  $Al_2(OH)_5Cl \cdot 2H_2O$ . Preferred zirconium compounds for preparation of such ZAG-type complexes are zirconyl hydroxychloride having the empirical formula  $ZrO(OH)Cl \cdot 3H_2O$  and the zirconyl hydroxyhalides of the empirical formula  $ZrO(OH)_{2-a}Cl_2 \cdot nH_2O$  wherein a is from about 1.5 to about 1.87, and n is from about 1 to about 7. The preferred amino acid for preparing such ZAG-type complexes is glycine of the formula  $CH_2(NH_2)COOH$ . Salts of such amino acids can also be employed in the antiperspirant complexes. See U.S. Patent 4,017,599 issued to Rubino on April 12, 1977.

A wide variety of other types of antiperspirant complexes are also known in the art. For example, U.S. Patent 3,903,258 issued to Siegal on September 2, 1975 discloses a zirconium aluminum complex prepared by reacting zirconyl chloride with aluminum hydroxide and aluminum chlorhydroxide. U.S. Patent 3,979,510 issued to Rubino on September 7, 1976 discloses an antiperspirant complex formed from certain aluminum compounds, certain zirconium compounds, and certain complex aluminum buffers. U.S. Patent 3,981,896 issued to Pauling on September 21, 1976 discloses an antiperspirant complex prepared from an aluminum polyol compound, a zirconium compound and an organic buffer. U.S. Patent 3,970,748 issued to Mecca on July 20, 1976 discloses an aluminum chlorhydroxy glycinate complex of the approximate general formula  $[Al_2(OH)_4Cl][H_2CNH_2COOH]$ .

Of all the above types of antiperspirant actives, preferred compounds include the 5/6 basic aluminum salts of the empirical formula  $Al_2(OH)_5Cl \cdot 2H_2O$ ;

mixtures of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$  with aluminum chloride to aluminum hydroxychloride weight ratios of up to about 0.5; ZAG type complexes wherein the zirconium salt is  $\text{ZrO}(\text{OH})\text{Cl} \cdot 3\text{H}_2\text{O}$ , the aluminum salt is  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$  or the aforementioned mixtures of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$  5 wherein the total metal to chloride molar ratio in the complex is less than about 1.25 and the Al:Zr molar ratio is about 3.3, and the amino acid is glycine; and ZAG-type complexes wherein the zirconium salt is  $\text{ZrO}(\text{OH})_{2-a}\text{Cl}_a \cdot n\text{H}_2\text{O}$  wherein a is from about 1.5 to about 1.87 and n is from about 1 to about 7, the aluminum salt is  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$ , and the amino acid is glycine.

10 Solubilized antiperspirant actives which can be utilized in the present invention are also well known in the art. These materials utilize monohydric or polyhydric alcohols or water to solublize the antiperspirant active before it is incorporated into the product. The levels of these polar solvents are typically less than about 25%, and preferably less than about 15% of the composition. 15 Examples of such actives are taught, for example, in U.S. Patent 4,137,306 issued to Rubino on January 30, 1979; U.S. Patent Application Serial No. 370,559, Smith and Ward, filed June 23, 1989; and European Patent Application 0295070 which published December 14, 1988, all of said patents and applications being incorporated herein by reference.

20

#### (v) Air Freshening Compositions

The air freshening composition of the present invention generally includes: from about 0.002% to about 1% of a malodor reducing composition of the present invention; and from about 0.01% to about 95% of a volatile solvent, 25 wherein the total amount of the amber chemical material and the musk material (1) in the malodor reducing composition is at least about 5% by weight; and (2) in the air freshening composition is from about 0.0001% to about 1%.

##### I. Volatile Solvent

30 The air freshening composition of the present invention generally includes volatile solvent. As used herein, the term "volatile solvent" includes any of the known volatile solvent, such as, exemplified in the section of "Balance Comprising Carrier".

35 The preferred volatile solvents are water, ethanol, isopropanol, pentane, hexane, and heptane. The water us ful herein include d ionized water and wat r from

natural sources containing mineral cations. Deionized water is preferred.

## II. Optional Ingredients for Air Freshening Compositions

Other components known to those skilled in the art can be utilized as  
5 optional ingredients for air freshening compositions of the present invention.

## C. Article of Manufacture for Consumer Products Containing Malodor Reducing Composition

The following description is non-limiting examples for manufacturing  
10 consumer products, especially for fabric freshening compositions, of the present invention. Other conventional article of manufacture known to those skilled in the art can be included as the article of manufacture for consumer product of the present invention.

### SPRAY DISPENSER

15 The article of manufacture herein comprises a spray dispenser. The composition of the present invention (e.g., fabric freshening composition) is placed into a spray dispenser in order to be distributed onto the surface of the material (e.g., fabric). Said spray dispenser is preferably any of the manually activated means for producing a spray of liquid droplets as is known in the art,  
20 e.g. trigger-type, pump-type, non-aerosol self-pressurized, and aerosol-type spray means. The spray dispenser herein does not normally include those that will substantially foam the clear, aqueous odor absorbing composition.

The spray dispenser can be an aerosol dispenser. Said aerosol dispenser comprises a container which can be constructed of any of the conventional materials employed in fabricating aerosol containers. The aerosol dispenser utilizes a pressurized sealed container from which the clear, aqueous odor-absorbing composition is dispensed through a special actuator/valve assembly under pressure. The aerosol dispenser is pressurized by incorporating therein a gaseous component generally known as a propellant. Common aerosol propellants, e.g., gaseous hydrocarbons such as isobutane, and mixed halogenated hydrocarbons, which are not preferred. Halogenated hydrocarbon propellants such as chlorofluoro hydrocarbons have been alleged to contribute to environmental problems. Preferred propellants are compressed air, nitrogen, inert gases, carbon dioxide, etc. A more complete description of commercially available aerosol-spray dispensers appears in U.S. Pat. Nos.: 3,436,772,

Stebbins, issued April 8, 1969; and 3,600,325, Kaufman et al., issued August 17, 1971; both of said references are incorporated herein by reference.

For a fabric freshening composition, preferably, the spray dispenser is a non-aerosol, manually activated, pump-spray dispenser. Said pump-spray 5 dispenser comprises a container and a pump mechanism which securely screws or snaps onto the container. The container comprises a vessel for containing the aqueous odor-absorbing composition to be dispensed.

The pump mechanism comprises a pump chamber of substantially fixed volume, having an opening at the inner end thereof. Within the pump chamber is 10 located a pump stem having a piston on the end thereof disposed for reciprocal motion in the pump chamber. The pump stem has a passageway there through with a dispensing outlet at the outer end of the passageway and an axial inlet port located inwardly thereof.

The container and the pump mechanism can be constructed of any 15 conventional material employed in fabricating pump-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyethyleneterephthalate; blends of polyethylene, vinyl acetate, and rubber elastomer. A preferred container is made of clear, e.g., polyethylene terephthalate. Other materials can include stainless steel. A more complete disclosure of commercially available 20 dispensing devices appears in: U.S. Pat. Nos.: 4,895,279, Schultz, issued January 23, 1990; 4,735,347, Schultz et al., issued April 5, 1988; and 4,274,560, Carter, issued June 23, 1981; all of said references are herein incorporated by reference.

Such spray dispenser can be a manually activated trigger-spray 25 dispenser. Said trigger-spray dispenser comprises a container and a trigger both of which can be constructed of any of the conventional material employed in fabricating trigger-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyacetal; polycarbonate; polyethyleneterephthalate; polyvinyl chloride; polystyrene; blends of polyethylene, vinyl acetate, and rubber 30 elastomer. Other materials can include stainless steel and glass. A preferred container can be made of clear, e.g. polyethylene terephthalate. The trigger-spray dispenser does not incorporate a propellant gas into the odor-absorbing composition, and preferably it does not include those that will foam the odor-absorbing composition. The trigger-spray dispenser herein is typically one which 35 acts upon a discrete amount of the odor-absorbing composition itself, typically by

means of a piston or a collapsing bellows that displaces the composition through a nozzle to create a spray of thin liquid. Said trigger-spray dispenser typically comprises a pump chamber having either a piston or bellows which is movable through a limited stroke response to the trigger for varying the volume of said 5 pump chamber. This pump chamber or bellows chamber collects and holds the product for dispensing. The trigger spray dispenser typically has an outlet check valve for blocking communication and flow of fluid through the nozzle and is responsive to the pressure inside the chamber. For the piston type trigger sprayers, as the trigger is compressed, it acts on the fluid in the chamber and the 10 spring, increasing the pressure on the fluid. For the bellows spray dispenser, as the bellows is compressed, the pressure increases on the fluid. The increase in fluid pressure in either trigger spray dispenser acts to open the top outlet check valve. The top valve allows the product to be forced through the swirl chamber and out the nozzle to form a discharge pattern. An adjustable nozzle cap can be 15 used to vary the pattern of the fluid dispensed.

For the piston spray dispenser, as the trigger is released, the spring acts on the piston to return it to its original position. For the bellows spray dispenser, the bellows acts as the spring to return to its original position. This action causes a vacuum in the chamber. The responding fluid acts to close the outlet valve 20 while opening the inlet valve drawing product up to the chamber from the reservoir.

A more complete disclosure of commercially available dispensing devices appears in U.S. Pat. Nos. 4,082,223, Nozawa, issued Apr. 4, 1978; 4,161,288, McKinney, issued Jul. 17, 1985; 4,434,917, Saito et al., issued Mar. 6, 1984; and 25 4,819,835, Tasaki, issued Apr. 11, 1989; 5,303,867, Peterson, issued Apr. 19, 1994; all of said references are incorporated herein by reference.

A broad array of trigger sprayers or finger pump sprayers are suitable for use with the compositions of this invention. These are readily available from suppliers such as Calmar, Inc., City of Industry, California; CSI (Continental 30 Sprayers, Inc.), St. Peters, Missouri; Berry Plastics Corp., Evansville, Indiana, a distributor of Guala® sprayers; or Seaquest Dispensing, Cary, Illinois.

#### D. Method of Using Consumer Products Containing Malodor Reducing Composition

35 The consumer products of the present invention are used in conventional

ways to provide the desired benefit appropriate to the product such as freshening fabrics, freshening air, freshening and styling hair, freshening and holding hair, freshening and cleaning household products, the like. Such methods of use depend upon the type of composition employed but generally involve application 5 of an effective amount of the product to the fabrics, households, hair or skin, which can then be allowed to remain on the surface of fabrics/households, (as in the case of fabric freshening compositions/ household cleaning compositions; allowed to remain on the hair (as in the case of spray, mousse, or gel products); or allowed to remain on the skin (as in the case of the antiperspirants/ 10 deodorants). By "effective amount" is meant an amount sufficient to provide the benefit desired.

The aspects and embodiments of the present invention set forth in this document have many surprising advantages, including providing malodor 15 reducing compositions which provide malodor impression on surfaces of, e.g., a including fabrics and hair, that are contaminated with environmental odors such as cigarette smoke odors, cooking smoke odors and/or that are wetted with perspiration, air in confined spaces such as bathrooms and kitchens and in consumer products which contain materials which are inherently malodorous, 20 with substantially no odor or faint odor impression on the surfaces after treating the compositions.

#### EXAMPLES

The following examples further describe and demonstrate the preferred 25 embodiments within the scope of the present invention. The Examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention as many variations thereof are possible without departing from its spirit and scope.

Eight different malodor reducing compositions are used in the following 30 examples. Compositions A thorough G are examples of malodor reducing compositions of this invention. Comparative Compositions H and I are compositions which are outside the scope of this invention.

		<u>Composition A</u> <u>(Wt. %)</u>	<u>Composition B</u> <u>(Wt. %)</u>	<u>Composition C</u> <u>(Wt. %)</u>
<u>Ingredients</u>				
	Cedroxyde	3	7	20
	Cedramber	2	3	5
	Oxalide	5	10	-
5	Exaltone	-	-	5
	Benzyl Salicylate	30	30	30
	Evernyl	3	3	3
	Hedione	30	20	20
	Methyl Eugenol	7	7	7
10	Ionone gamma Methyl	20	20	10
	Total	100	100	100

		<u>Composition D</u> <u>Ingredients</u>	<u>Composition E</u> <u>(Wt.%)</u>	<u>Composition F</u> <u>(Wt.%)</u>
	Ambroxan	1	1	1
5	Galaxolide - 50%(1)	20	20	40
	Tonalide	40	40	-
	Celestolide	-	-	20
	Pentalide	3	3	-
	Oxalide	2	2	1
10	Musk T	-	-	9
	Exaltone	-	-	5
	Benzyl Salicylate	10	10	-
	Hexyl Salicylate	2	2	-
	Evermyl	-	-	2
15	Hedione	20	10	20
	Methyl Eugenol	2	2	2
	Dihydro Myrcenol	-	5	-
	Lavandin Grosso	-	3	-
	cis-3-Hexenol	-	1.5	-
20	Allyl Amyl Glycolate	-	0.5	-
	Total	100	100	100

(1) A 50% solution in benzyl benzoate

		<u>Composition G</u>	<u>Comparative Composition H</u>
	<u>Ingredients</u>	<u>(Wt.%)</u>	<u>(Wt.%)</u>
5	Ambroxan	2	-
	Hydroxyambran	3	-
	Tonalide	30	-
	Pentalide	3	-
	Oxalide	2	-
10	Benzyl Salicylate	10	-
	Hedione	10	20
	Hyrdoxycitronellal	10	20
	Phenoxyethanol	5	10
	Helional	5	10
15	Dipentene	5	10
	alpha Pinene	15	30
	Total	100	100

20

		<u>Comparative Composition I</u>
	<u>Perfume Ingredients</u>	<u>(Wt.%)</u>
	Diphenyl Oxide	25
	Beta Naphthol Methyl Ether	25
25	Allyl Cyclohexan Propionate	25
	Amyl Cinnamic Aldehyde	25
	Total	100

EXAMPLES I-VII, COMPARATIVE EXAMPLES VIII-XIX:

## (Fabric Freshening Compositions)

5        The following Examples I thorough VII exemplify fabric freshening compositions of the present invention. Comparative Examples VIII and XIX are compositions which are outside the scope of this invention.

10      The compositions used for the examples and comparative examples, were prepared by mixing and dissolving the ingredients into clear solutions. Each of 10 the compositions were packed into Spray Vial No.6 (an atomizing spray vial, commercially available from Maruemu Corporation in Japan).

	<u>Ingredients</u>	<u>Example I</u>	<u>Example II</u>	<u>Example III</u>
		(Wt.%)	(Wt.%)	(Wt.%)
15	HPBCD(1)	1.0	1.0	1.0
	ZnCl <sub>2</sub>	1.0	1.0	1.0
	Silwet L-7600(2)	0.15	0.15	0.15
	Propylene Glycol	0.06	0.06	0.06
	Kathon(antimicrobial)	3ppm	3ppm	3ppm
20	HCL	to pH 4	to pH 4	to pH 4
	Composition A (20%)	0.03	-	-
	Composition B (20%)	-	0.03	-
	Composition C (20%)	-	-	0.03
25	Water	—————Balance to 100—————		

<u>Ingredients</u>	<u>Example IV</u>	<u>Example V</u>	<u>Example VI</u>	<u>Example VII</u>
	(Wt.%)	(Wt.%)	(Wt.%)	(Wt.%)
HPBCD(1)	1.0	1.0	1.0	1.0
ZnCl <sub>2</sub>	1.0	1.0	1.0	1.0
Silwet L-7600(2)	0.15	0.15	0.15	0.15
Propylene Glycol	0.06	0.06	0.06	0.06
Kathon	3ppm	3ppm	3ppm	3ppm
HCL	to pH 4	to pH 4	to pH 4	to pH 4
Composition D (20%)	0.03	-	-	-
Composition E (20%)	-	0.03	-	-
Composition F (20%)	-	-	0.03	-
Composition G (20%)	-	-	-	0.03
Water	-----	Balance to 100	-----	-----

<u>Ingredients</u>	<u>Comparative Example V</u>	<u>Comparative Example VI</u>
	(Wt.%)	(Wt.%)
HPBCD(1)	1.0	1.0
ZnCl <sub>2</sub>	1.0	1.0
Silwet L-7600(2)	0.15	0.15
Propylene Glycol	0.06	0.06
Kathon	3ppm	3ppm
HCL	to pH 4	to pH 4
Comparative Comp.H (20%)	0.03	-
Comparative Comp.I (20%)	-	0.03
Water	-----	Balance to 100-----

- (1) Hydroxypropyl beta-cyclodextrin  
(2) Cyclodextrin-compatible nonionic surfactant, supplied by OSi Specialities, Inc.

5

All the Compositions A thorough I used as a 20% solution in 2-ethoxyethanol which is not counted in the composition.

Procedures of Odor Evaluations:

10

Odor evaluations for three different kinds of malodors on fabric were conducted by following procedures.

Preparations for Fabric Swatches with Different Kinds of Malodors:

15

• Cigarette Smoke Odor:

20

25

1. Prepare swatches of white poly-cotton (60 cotton/40 polyester) fabric.  
(Size: 8 inch x 8 inch, weight: ~8.4g).
2. Place the lighted one cigarette in a lidded container.
3. Hang the swatches on the lid of the container over the cigarette in the trash can.
4. Time to 60 seconds.
5. Close the lid tightly and let the smoke absorbed by the swatches.
6. Take the swatches out from the can and store them in a plastic bag.
7. Store the swatches in a plastic bag to keep the odor and avoid contamination until technical evaluations.

• Cooking Smoke Odor:

30

1. Prepare swatches of white poly-cotton (60 cotton/40 polyester) fabric.  
(Size: 8 inch x 8 inch, weight: ~8.4g).
2. Place the swatches on a table counter in a restaurant which is filled with cooking smoke for one hour while cooking so the odor from cooking can be absorbed by the swatches.
3. Store the swatches in a plastic bag to keep the odor and avoid contamination until technical evaluations.

- Body (Worn T-shirt) Odor:

1. Prepare 100% cotton T-shirts.
2. T-shirt are worn for a whole day so the odor of body can be absorbed by the T-shirt.
3. Cut the worn T-shirt into 8 inch x 8 inch size swatches.
4. Store the swatches in a plastic bag to keep the odor and avoid contamination until technical evaluations.

5        10      Technical Odor Evaluations: (Done by at least three sensory evaluators in an odor free room.)

1. Smell all the swatches to measure malodor impact using a 0-100 scale below and select the one with the same impact.
2. Spray 0.6 g of Febreze on the four corners and center of a swatch.
- 15      3. Smell swatch to measure perfume and malodor impact for "wet fabric" using a 0-100 odor impact scale. (See the definition of the scale below.)
4. Hang swatches on a drying line in an odor-free room.
5. Smell swatch 1.5 hours later to measure perfume and malodor impact for "dry down" using the 0-100 odor impact scale.

20

Odor Impact Scale:

- |             |                                |
|-------------|--------------------------------|
| 0:          | No odor                        |
| 10:         | I think there is odor (unsure) |
| 25:         | Slight odor                    |
| 25      50: | Moderate odor                  |
| 75:         | Strong odor                    |
| 100:        | Extremely strong odor          |

Results of Odor Evaluation:

	Example I		Example II		Example III	
	Malodor	Perfume	Malodor	Perfume	Malodor	Perfume
	Odor	Odor	Odor	Odor	Odor	Odor
<b>Cigarette Smoke Odor</b>						
5	Initial	85	-	85	-	85
	Wet Fabric	60	60	60	55	60
	Dry Fabric	5	20	5	20	5
<b>Cooking Smoke Odor</b>						
10	Initial	75	-	75	-	75
	Wet Fabric	55	55	55	50	50
	Dry Fabric	30	10	30	10	10
<b>Body Odor</b>						
15	Initial	70	-	70	-	70
	Wet Fabric	55	50	50	50	50
	Dry Fabric	15	20	15	20	20
<b>Cigarette Smoke Odor</b>						
20	Initial	85	-	85	-	85
	Wet Fabric	70	50	60	60	70
	Dry Fabric	5	20	5	20	0
<b>Cooking Smoke Odor</b>						
25	Initial	75	-	75	-	75
	Wet Fabric	65	50	55	60	55
	Dry Fabric	35	10	25	15	30

Body Odor						
	Initial	70	-	70	-	70
5	Wet Fabric	55	50	50	60	60
	Dry Fabric	25	15	25	20	25
	<u>Example VII</u>		<u>Comparative</u>		<u>Comparative</u>	
	<u>Example VIII</u>		<u>Example IX</u>			
	<u>Malodor</u>	<u>Perfume</u>	<u>Malodor</u>	<u>Perfume</u>	<u>Malodor</u>	<u>Perfume</u>
	<u>Odor</u>		<u>Odor</u>		<u>Odor</u>	
Cigarette Smoke Odor						
	Initial	85	-	85	-	85
10	Wet Fabric	50	70	75	65	50
	Dry Fabric	5	20	40	15	0
Cooking Smoke Odor						
	Initial	75	-	75	-	75
15	Wet Fabric	55	70	65	65	60
	Dry Fabric	20	15	60	10	30
Body Odor						
	Initial	70	-	70	-	70
20	Wet Fabric	50	65	65	65	30
	Dry Fabric	30	20	55	15	40

As shown above, the fabric freshening compositions of the present invention comprising malodor reducing composition (Examples I-VII) showed better performance, especially after drying, e.g., reducing malodor without noticeable perfume odor, than the compositions of Comparative Examples VIII-IX.

#### EXAMPLES X-XII:

(Fixative Hair Spray and Mousses)

30 The compositions of Examples X thorough XII as shown below can be prepared by any conventional method well known in the art. Suitable methods are described below.

The fixative hair spray of Example X is suitably made as follows: Hair fixative polymer is dissolved in a portion of water and ethanol. To this is added the remaining components except isobutane/propane blend. The obtained mixture is mixed until homogeneous. Finally, the concentrate thus obtained is packed into an aerosol can with isobutane/propane blend.

The hair mousse of Examples XI and XII are suitably made as follows: Hair fixative polymer is dissolved in a portion of water. To this is added the remaining ingredients except isobutane/propane blend. The obtained mixture is mixed until homogeneous. The concentrate thus obtained is packed into an aerosol can with isobutane/propane blend.

<u>Ingredients</u>	<u>Ex.X (Wt.%)</u>	<u>Ex.XI (Wt.%)</u>	<u>Ex.XII (Wt.%)</u>
Denatured Ethyl Alcohol	73.25	7.50	7.50
Composition A (100%)	0.10	-	-
Composition B (100%)	-	0.05	-
Composition C (100%)	-	-	0.05
Polyacrylic acid-co-ethyl acrylate- co-t-butyl acrylamide(1)	6.00	-	-
Polyoctylacrylamide-co- alkyacrylate-co-butylaminoethyl methacrylate(2)	-	4.00	4.00
Aminomethyl propanol(3)	0.15	0.70	0.70
Dimethicone copolyol(4)	0.10	-	-
Lauramide DEA	0.10	-	-
Laureth-23	-	0.20	0.20
Laureth-7	-	0.10	0.10
Propylene glycol	-	0.10	0.10
Preservatives	-	0.10	0.10
Isobutane/propane	-	7.00	7.00
Water	Balance to 100		

#### Definitions

15 (1) Polyacrylic acid-co-ethyl acrylate-co-t-butyl acrylamide: Ultrahold-8

- obtained by BASF
- (2) Polyoctylacrylamide-co-alkyacrylate-co-butylaminoethyl methacrylate:  
Amphomer 28-4910 obtained by National Starch
- (3) Aminomethylpropane: AMP-regular obtained by Angus.
- 5 (4) Dimethicone copolyol: SH3746 obtained by Dow Corning

**COMPARTIVE EXAMPLE XIII:**

Fixative hair spray composition of the Comparative Example XIII which is outside of the scope of the present invention is made similarly to that of Example 10 XI, except that the Comparative Composition H is used instead of Composition B. Hair worked with the composition of the Comparative Example XIII noticeably less malodor reduction and more perfume odor than when the composition of Example XI is used.

15 **EXAMPLES XIV-XV:**

(Compositions for Cleaning Typical Household Surfaces)

The compositions of Examples XIV thorough XV as shown below can be prepared by any conventional method well known in the art. The hydrogen peroxide is separated as an aqueous solution from the other components by any 20 suitable means, such as dual-chamber container.

<u>Ingredients</u>	<u>Ex.XIV</u> <u>(Wt.%)</u>	<u>Ex.XV</u> <u>(Wt.%)</u>
C <sub>8</sub> -10E <sub>6</sub> Nonionic surfactant	20	15
C <sub>12</sub> -13E <sub>3</sub> Nonionic surfactant	4	4
C <sub>8</sub> Alkyl sulfate anionic surfactant	0	7
Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub>	1	2
C <sub>12</sub> -18 Fatty Acid	0.6	0.4
Hydrogen peroxide	7	7
N-benzoyl-3-oxmorpholine	7	7
Dequest 2060(1)	0.05	0.05
Composition D (100%)	0.1	0.1
Water	————Balance to 100————	

(1) Commercially available from monsanto Co.

COMPARATIVE EXAMPLE XVI:

The compositions for cleaning typical household surfaces of the  
 5 Comparative Example XVI which is outside the scope of the present invention is made similarly to that of Example XIV, except that the Comparative Composition H is used instead of Composition D. The household surface worked with the composition of the Comparative Example XVI has noticeably less malodor reduction and more perfume odor than when the composition of Example XIV is  
 10 used.

EXAMPLES XVII-XXI:

(Antiperspirant Composition)

The compositions of Examples XVII thorough XXI as shown below can be  
 15 prepared by any conventional method well known in the art.

	<u>Ex.</u> <u>XVII</u>	<u>Ex.</u> <u>XVIII</u>	<u>Ex.</u> <u>XIX</u>	<u>Ex.</u> <u>XX</u>	<u>Ex.</u> <u>XXI</u>
<u>Ingredients</u>	<u>(Wt.%)</u>	<u>(Wt.%)</u>	<u>(Wt.%)</u>	<u>(Wt.%)</u>	<u>(Wt.%)</u>
N-Lauroyl-L-glutamic acid-di-n-butyl amide(1)	4	1	2	2	1
12-hydroxystearic acid	2	5	7	6	12
Cyclomethicone D-5(2)	-	49	43	43	46
Polyphenylmethylsiloxane(3)	-	-	-	5	-
Light mineral oil(4)	23	-	-	-	-
Panalane-L-14E(5)	-	10	-	-	-
Isopropyl Myristate	-	15	-	11	-
Isopropyl Alcohol	-	-	18	-	-
C <sub>12</sub> C <sub>15</sub> Alcohols Benzoate(6)	-	-	-	8	-
PPG-3 Myristyl Ether	-	-	-	-	26
Diisopropyl Sebacate(7)	43	-	-	-	-
Aluminum Zirconium Trichlorhydrex Gly(8)	24.9	19.9	-	24.8	-
35 Aluminum Chlorohydrate(9)	-	-	29.86	-	9.85

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	Composition F (100%)	0.1	0.01	0.2	-
	Composition C (100%)	-	-	0.14	-
	Talc	3	-	-	5
5	Total	100	100	100	100

- (1) GP-1 supplied by Ajinomoto, Inc.
- (2) Dow Corning 245 Fluid-cyclic polydimethylsiloxane
- (3) Dow Corning 556 Fluid
- 10 (4) Benol White Mineral Oil supplied by Witco Chemical Corp.
- (5) Polyisobutene supplied by Amoco Chemical Company
- (6) Finsolv® TN supplied by Finetex
- (7) Schercemol® DIS supplied by Scher Chemicals Inc.
- (8) Supplied by Westwood Chemical Co.
- 15 (9) Westchlor® DM200 supplied by Westwood Chemical Co.

**COMPARTIVE EXAMPLE XXII:**

The antiperspirant composition of the Comparative Example XXII which is outside the scope of the present invention is made similarly to that of Example XVII, except that the Comparative Composition H is used instead of Composition F. The object worked with the composition of the Comparative Example XXII has noticeably less malodor reduction and more perfume odor than when the composition of Example XVII is used.

**EXAMPLE XXIII:**

(Deodorant Composition)

The composition of Example XXIII as shown below can be prepared by any conventional method well known in the art.

30		<u>Ex.XXIII</u>
	<u>Ingredients</u>	<u>(Wt. %)</u>
	Cyclomethicone D-5 (1)	39.8
	Light Mineral Oil (2)	11.5
35	Dimethicone (50 csk) (3)	1.5

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	Stearyl Alcohol	14.0
	Hydrogenated Castor Oil (4)	4.5
	Eicosanol	0.2
	Talc	1.4
5	Fumed Silica (5)	1.0
	Composition D (100%)	0.1
	Aluminum Chlorohydrate (6)	26.0
	<hr/>	
	Total	100
10		
	(1) A 5 carbon cyclic polydimethylsiloxane supplied by G.E. Silicones	
	(2) Benol White Mineral Oil, supplied by Witco Chemical Corporation (viscosity = 18-20 csk at 40°C; density = 0.839-0.855 g/cm3)	
	(3) Supplied by Dow Corning	
15	(4) Castor Wax MP 80, supplied by NL Industries	
	(5) Cab-O-Sil HS-5, supplied by Cabot Corporation	
	(6) Reheis 501 macrospherical aluminum chlorohydrate, supplied by Reheis Chemical Company	

20 COMPARTIVE EXAMPLE XXIV:

The antiperspirant composition of the Comparative Example XXIV which is outside of the scope of the present invention is made similarly to that of Example XXIII, except that the Comparative Composition H is used instead of Composition D. The object worked with the composition of the Comparative Example XXIV has noticeably less malodor reduction and more perfume odor than when the composition of Example XXIII is used.

EXAMPLE XXV:

(Air Freshening Composition)

30 The composition of Example XXV as shown below can be prepared by any conventional method well known in the art.

<u>Ingredients</u>	<u>Ex.XXV</u>
	<u>(Wt. %)</u>

Ethanol	39.9
n-Pentane	20.0
Dimethylether	40.0
Composition D (100%)	0.1
5	_____
Total	100

COMPARTIVE EXAMPLE XXVI:

The air freshening composition of the Comparative Example XXVI which is outside the scope of the present invention is made similarly to that of Example XXV, except that the Comparative Composition H is used instead of Composition D. The object worked with the composition of the Comparative Example XXVI has noticeably less malodor reduction and more perfume odor than when the composition of Example XXV is used.

15

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

**WHAT IS CLAIMED IS:**

1. A composition comprising :
  - (A) an amber chemical material; and
  - (B) a musk material;

wherein the total amount of the amber chemical material and the musk material in the composition is at least about 5 % by weight, and wherein the weight ratio of the the amber chemical material to the musk material in the composition is from about 100:1 to about 1:100.
2. A consumer product comprising the composition of Claim 1,  
wherein the total amount of the amber chemical material and the musk material in the consumer product is from about 0.0001% to about 1%, and wherein the weight ratio of the the amber chemical material to the musk material in the consumer product is from about 100:1 to about 1:100.
3. A household cleaning composition comprising:
  - (i) from about 0.002% to about 1% by weight of a malodor reducing composition;
  - (ii) from about 0.01% to about 60% by weight of a surfactant system;
  - (iii) an adjunct ingredient selected from the group consisting of abrasives, builders, bleaches, bleach boosters, bleach activators, clays, thickeners, dispersants, enzymes, dyes, colorants, filler salts, hydrotropes, enzymes, preservatives, anti-oxidants, chelants, stabilizers, germicides, fungicides, solvents, photodisinfectants, and mixtures thereof;

from about 0.01% to about 30% by weight of a bleaching agent; and

  - (iv) the balance comprising carrier,

wherein the malodor reducing composition having;

  - (A) an amber chemical material; and
  - (B) a musk material;

wherein the total amount of the amber chemical material and the musk material in the malodor reducing composition is at least about 5 % by weight, and wherein the weight ratio of the the amber chemical material to the musk material in the malodor reducing composition is from about 100:1 to about 1:100.

4. A fabric freshening composition comprising:

(i) from about 0.002% to about 1% by weight of a malodor reducing composition;

(ii) from about 0.01% to about 5% by weight of a cyclodextrin selected from the group consisting of cyclodextrins containing from 6 to 12 glucose units, derivatives thereof and mixtures thereof; and

(iii) the balance comprising carrier,

wherein the malodor reducing composition having;

(A) an amber chemical material; and

10 (B) a musk material;

wherein the total amount of the amber chemical material and the musk material in the malodor reducing composition is at least about 5 % by weight, and wherein the weight ratio of the the amber chemical material to the musk material in the malodor reducing composition is from about 100:1 to about 1:100.

15

5. An air freshening composition comprising:

(i) from about 0.002% to about 1% by weight of a malodor reducing composition; and

(ii) from about 0.01% to about 95% by weight of a volatile solvent ,

5 wherein the malodor reducing composition having;

(A) an amber chemical material; and

(B) a musk material;

wherein the total amount of the amber chemical material and the musk material in the malodor reducing composition is at least about 5 % by weight, and wherein

10 the weight ratio of the the amber chemical material to the musk material in the malodor reducing composition is from about 100:1 to about 1:100.

6. A hair treating composition comprising:

(i) from about 0.002% to about 1% by weight of a malodor reducing composition;

(ii) from about 0.01% to about 10% by weight of a fixative polymer; and

5 (iii) the balance comprising carrier,

wherein the malodor reducing composition having;

(A) an amber chemical material; and

(B) a musk material;

wherein the total amount of the amber chemical material and the musk material in the malodor reducing composition is at least about 5 % by weight, and wherein the weight ratio of the the amber chemical material to the musk material in the malodor reducing composition is from about 100:1 to about 1:100.

7. An antiperspirants composition comprising:

- (i) from about 0.002% to about 1% by weight of a malodor reducing composition;
- (ii) from about 0.01% to about 95% by weight of a surfactant system; and
- (iii) the balance comprising carrier,

wherein the malodor reducing composition having;

- (A) an amber chemical material; and
- (B) a musk material;

wherein the total amount of the amber chemical material and the musk material in the malodor reducing composition is at least about 5 % by weight, and wherein the weight ratio of the the amber chemical material to the musk material in the malodor reducing composition is from about 100:1 to about 1:100.

8. The composition of Claims 1, 3, 4, 5, 6 or 7 wherein the amber chemical material is selected from the group consisting of: 3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan, 6,6,9a-trimethyl-3a-

ethyldodecahydronaphtho[2,1-b]furan, 2-ethoxy-9-methylene-2,6,6-

5 trimethylbicyclo[3.3.1]nonane, 2-(cyclododecyl)-propan-1-ol, 7-acetyl-1,2,3,4,5,6,7,8,-octahydro-1,1,6,7-tetramethylnaphthalene, methyl 2,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone, 2,5,5-trimethyl-1,2,3,4,4a,5,6,7-octahydro-2-naphtalenol, 1-(2,2,6-trimethylcyclohexyl)-3-hexanol,  $\alpha,\beta$ ,2,2,6-pentamethylcyclohexylpropanol, 6,7,-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone, 3-oxabicyclo[10.3.0]pentadec-6-ene, 13-

10 oxabicyclo[10.3.0]pentadecane, 1-methyl-1-methoxycyclododecane, 4,8,12-trimethyl-13-oxabicyclo-[10.1.0]trideca-4,8-diene, ethoxy methylcyclododecyl ether, cedryl methyl ether, 2,4-dimethyl-2-(1,1,4,4-tetramethyltetralin-6yl)-1,3-dioxolane, and mixtures thereof.

15

9. The composition of Claims 1, 3, 4, 5, 6 or 7 wherein the musk material is selected from the group consisting of: 3-methylcyclodecanone, 9-

cyclopentadecen-1-one, cyclopentadecanone, 5-cyclohexadecen-1-one,  
cyclopentadecanolide, 12-ketocyclopentadecanolide, cyclohexadecanolide, 7-  
5 cyclohexadecenolide, 12-oxa-16-hexadecanolide, 11-oxa-16-hexadecanolide,  
10-oxa-16-hexadecanolide, ethylene brassylate, ethylene dodecanoate, 6-  
acetyl-1,1,2,3,3,5-hexamethylindane, 4-acetyl-6-t-butyl-1,1-dimethylindane, 5-  
acetyl-3-isopropyl-1,1,2,6-tetramethylindane, 6-acetyl-1,1,2,4,4,7-  
hexamethyltetralin, 4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-  
10 hexahydrocyclopentabenzopyran, 2,6-dinitro-3,5-dimethyl-4-t-butylbenzene,  
2,4,6-trinitro-5-t-butylbenzene, 2,6-dinitro-3-methoxy-1-methyl-4-t-butylbenzene,  
2,6-dinitro-3,4,5-trimethyl-t-butylbenzene, 1,1,3,3,5-pentamethyl-4,6-  
dinitroindane, and mixtures thereof.

10. The composition of Claim 1 wherein the composition further comprises a  
solubilizing agent selected from the group consisting of: water; C1-C4  
monohydric alcohols; C2-C6 polyhydric alcohols; propylene carbonate; liquid  
polyalkylene glycols; triethyl citrate; isopropyl myristate; benzyl benzoate; and  
5 mixtures thereof.

11. The composition of Claims 1, 3, 4, 5, 6 or 7 wherein the weight ratio of the  
amber chemical material to the musk material in the composition is from about  
5:1 to 1:60.

12. The composition of Claims 1, 3, 4, 5, 6 or 7 wherein the musk material has  
a ClogP of not less than 3.5.

13. The composition of Claim 2 wherein the salicylate esters are selected from  
the group consisting of: ethyl salicylate, isoamyl salicylate, hexyl salicylate, cis-3-  
hexenyl salicylate, benzyl salicylate, phenyl ethyl salicylate and mixtures thereof.

# INTERNATIONAL SEARCH REPORT

Inte  
ional Application No  
PCT/US 97/16751

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>	IPC 6 A61K7/32	A61K7/46	A61L9/01	C11B9/00	C11D3/50
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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K A61L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 970 593 A (NAGAKURA AKIRA ET AL) 20 July 1976 see column 1, line 67 - column 2, line 20 see column 3, line 4 - line 16 ---	1,2
X	DE 41 41 097 A (SCHMITZ GOEBBELS SABINE) 3 June 1993 see column 1, line 62 - column 2, line 7 see claims 1,7,8,12 ---	1,2
Y	EP 0 557 419 A (PROCTER & GAMBLE) 1 September 1993 see page 2, line 41 - page 3, line 8 see page 5, line 12 - line 35 see page 7, line 3 - line 21 see page 7, line 48 - page 8, line 17 ---	3,5,10
X	EP 0 557 419 A (PROCTER & GAMBLE) 1 September 1993 see page 2, line 41 - page 3, line 8 see page 5, line 12 - line 35 see page 7, line 3 - line 21 see page 7, line 48 - page 8, line 17 ---	1-3,8,9, 12
Y	EP 0 557 419 A (PROCTER & GAMBLE) 1 September 1993 see page 2, line 41 - page 3, line 8 see page 5, line 12 - line 35 see page 7, line 3 - line 21 see page 7, line 48 - page 8, line 17 ---	4,6,7,10
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search

Date of mailing of the international search report

10 February 1998

16.02.98

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Authorized officer

Heck, G

**INTERNATIONAL SEARCH REPORT**

Inte onal Application No
PCT/US 97/16751

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 596 493 A (NIPPON PEROXIDE CO LTD) 11 May 1994 see abstract see page 2, line 39 - line 42 see page 2, line 54 - page 3, line 15 see page 4, line 37 - page 5, line 11 -----	3,10
Y	US 5 578 563 A (TRINH TOAN ET AL) 26 November 1996 see abstract see column 4, paragraph 3 - column 7, paragraph 1 see column 9, line 41 - line 51 see column 11, line 38 - line 47 -----	4,10
Y	US 4 810 690 A (DUMAS SYLVIE) 7 March 1989 see claims 1,4,5 -----	5,10
Y	EP 0 635 257 A (NAT STARCH CHEM INVEST) 25 January 1995 see page 3, line 21 - line 28 see example 1 see claim 1 -----	6,10
Y	US 5 603 925 A (ROSS LLOYD ET AL) 18 February 1997 see column 6, line 26 - line 43 see column 10, line 36 - line 45 see example 3 see claim 1 -----	7,10

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/16751

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2.  Claims Nos.: 13 because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
**Lack of clarity:** The salicylate esters in claim 13 are not mentioned in any of the previous claims
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte	onal Application No
PCT/US 97/16751	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 3970593 A	20-07-76	JP 1039192 C JP 50100247 A JP 55030686 B CA 1042451 A CH 590858 A DE 2461594 A FR 2257590 A GB 1453912 A NL 7416928 A,B		31-03-81 08-08-75 13-08-80 14-11-78 31-08-77 17-07-75 08-08-75 27-10-76 15-07-75
DE 4141097 A	03-06-93	NONE		
EP 0557419 A	01-09-93	DE 69116572 D DE 69116572 T JP 6502669 T AT 133195 T AU 9053891 A CA 2096254 A CN 1062375 A ES 2082445 T MX 9102021 A NZ 240572 A TR 26092 A WO 9208780 A		29-02-96 19-09-96 24-03-94 15-02-96 11-06-92 15-05-92 01-07-92 16-03-96 29-04-94 22-12-94 15-12-94 29-05-92
EP 0596493 A	11-05-94	JP 6145696 A US 5451346 A		27-05-94 19-09-95
US 5578563 A	26-11-96	CA 2197442 A EP 0774979 A WO 9604938 A		22-02-96 28-05-97 22-02-96
US 4810690 A	07-03-89	FR 2601592 A AU 586344 B AU 7552887 A CA 1290696 A DK 376887 A,B, EP 0254621 A FI 88584 C GB 2192791 A,B		22-01-88 06-07-89 28-01-88 15-10-91 22-01-88 27-01-88 10-06-93 27-01-88

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4810690 A		IE 60926 B ZA 8705169 A	07-09-94 20-01-88
EP 0635257 A	25-01-95	US 5599524 A AT 158715 T CA 2128313 A DE 69405927 D JP 2531934 B JP 7145024 A	04-02-97 15-10-97 22-01-95 06-11-97 04-09-96 06-06-95
US 5603925 A	18-02-97	AU 5449296 A WO 9632924 A	07-11-96 24-10-96